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TOKUNAGA MASAOKI(54) RARE-EARTH MAGNET MATERIAL, ITS MANUFACTURE, AND RARE-EARTH BOND
MAGNET USING IT

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a magnet material having a peculiar large coercive force which has a small temperature coefficient by forming a crystalline structure containing monoclinic and/or hexagonal $R_3(Fe, M, B)_{29}Ny$ as a main phase by using an R-Fe-B-N magnet material having a specific ratio of components.

SOLUTION: A rare-earth magnet material has a composition of $R_\alpha Fe_{100-(\alpha+\beta+\gamma+\delta)} M_\beta B_\gamma N_\delta$ containing monoclinic and/or hexagonal $R_3(Fe, M, B)_{29}Ny$ as a main phase. The R and Y respectively represent one or two or more kinds of rare-earth elements including Y and one or two or more kinds of elements selected from among Al, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, and W and the α , β , γ , and δ are atomic percentages respectively set at $5 \leq \alpha \leq 18$, $1 \leq \beta \leq 50$, $0.1 \leq \gamma \leq 5$, and $4 \leq \delta \leq 30$. Therefore, a rare-earth magnet material and a bond magnet having high Curie temperatures and high thermal stability can be obtained.

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CLAIMS

[Claim(s)]

[Claim 1] A component presentation is $R\alpha\beta\gamma\delta$ $M\beta\gamma\delta$ $R_3(Fe, M, B)_{29}N_y$ with the monoclinic system and/or hexagonal crystal structure is included as a main phase. Said R is any one sort of the rare earth elements including Y, or two sorts or more. It is the rare earth magnet ingredient which said M consists of any one sort of aluminum, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, and the W, or two sorts or more, and is characterized by the range following with atomic percent having Above α , β , γ , and δ .

$5 \leq \alpha \leq 181 \leq \beta \leq 500.1 \leq \gamma \leq 54 \leq \delta \leq 30$ -- [Claim 2] A component presentation is $R\alpha\beta\gamma\delta\epsilon\zeta$ $M\beta\gamma\delta\epsilon\zeta$ $R_3(Fe, M, B)_{29}N_y$ with the monoclinic system and/or hexagonal crystal structure is included as a main phase. Said R is any one sort of the rare earth elements containing Y, or two sorts or more. It is the rare earth magnet ingredient which said M consists of any one sort of aluminum, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, and the W, or two sorts or more, and is characterized by the range following with atomic percent having Above α , β , γ , δ , ϵ , and ζ .

$5 \leq \alpha \leq 181 \leq \beta \leq 500.1 \leq \gamma \leq 54 \leq \delta \leq 300.5 \leq \epsilon \leq 101 \leq \zeta \leq 5$ -- [Claim 3] The rare earth magnet ingredient according to claim 1 or 2 characterized by permuting 0.01 - 30 atom % of Fe component with Co and/or nickel.

[Claim 4] The rare earth magnet ingredient according to claim 1 to 3 characterized by more than 50 atom % of R component being Sm.

[Claim 5] The rare earth magnet ingredient according to claim 1 to 4 with which mean particle diameter of a rare earth magnet ingredient is characterized by 20-micrometer or more being 500 micrometers or less.

[Claim 6] The rare earth magnet ingredient according to claim 1 to 5 characterized by

having the organization where M element or M compound deposited in the crystal grain of an R₃ (Fe, M, B)₂₉Ny phase.

[Claim 7] The rare earth magnet ingredient according to claim 1 to 6 characterized by the rate of an abundance ratio of the R₃ (Fe, M, B)₂₉Ny phase in a rare earth magnet ingredient being more than 60 volume %.

[Claim 8] The rare earth magnet ingredient characterized by the proper coercive force (iH_c) in 25 degrees C being 8 or more kOes while it is the rare earth magnet ingredient with which it is combined by a giant-molecule polymer, a pure metal, or the alloy, and the magnet powder constitutes a bond magnet and the temperature coefficient (eta) of the proper coercive force (iH_c) in 25-100 degrees C of said magnet powder is -0.45 or more.

[Claim 9] A component presentation is R_{alpha}Fe_{100-(alpha+beta+gamma+delta)}M_{beta}B_{gamma}N_{delta}. R₃ (Fe, M, B)₂₉Ny with the monoclinic system and/or hexagonal crystal structure is included as a main phase. Said R is any one sort of the rare earth elements including Y, or two sorts or more. Said M aluminum, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, It consists of any one sort of Hf, Ta, and the W, or two sorts or more. Above alpha and beta, gamma and delta the powder of the rare earth magnet ingredient in the range following with atomic percent A macromolecule polymer, It is the rare earth bond magnet combined with either binder of a pure metal and an alloy. The rare earth bond magnet characterized by the coercive force (bH_c) in 25 degrees C being 6 or more kOes while the temperature coefficient (eta) of the proper coercive force (iH_c) in 25-100 degrees C of said bond magnet is -0.45 or more.

5<=alpha<=181<=beta<=500.1<=gamma<=54<=delta<=30 -- [Claim 10] A component presentation is R_{alpha}Fe_{100-(alpha+beta+gamma+delta+epsilon+zeta)}M_{beta}B_{gamma}N_{delta}H_{epsilon}O_{zeta}. R₃ (Fe, M, B)₂₉Ny with the monoclinic system and/or hexagonal crystal structure is included as a main phase. Said R is any one sort of the rare earth elements containing Y, or two sorts or more. Said M aluminum, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, It consists of any one sort of Hf, Ta, and the W, or two sorts or more. Above alpha and beta, gamma, delta, epsilon, and zeta the powder of the rare earth magnet ingredient in the range following with atomic percent It is the rare earth bond magnet combined with one binder of a giant-molecule polymer, a pure metal, and an alloy. The rare earth bond magnet characterized by the coercive force (bH_c) in 25 degrees C being 6 or more kOes while the temperature coefficient (eta) of the proper coercive force (iH_c) in 25-100 degrees C of said bond magnet is -0.45 or more.

5<=alpha<=181<=beta<=500.1<=gamma<=54<=delta<=300.5<=epsilon<=101<=zeta<=5 -- [Claim 11] A component presentation is R_{alpha}Fe_{100-(alpha+beta+gamma+delta)}

MbetaBgammaNdelta. R3 (Fe, M, B)29Ny with the monoclinic system and/or hexagonal crystal structure is included as a main phase. Said R is any one sort of the rare earth elements including Y, or two sorts or more. Said M consists of any one sort of aluminum, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, and the W, or two sorts or more, and Above alpha, beta, gamma, and delta is faced manufacturing the rare earth magnet ingredient in the range following with atomic percent. The manufacture approach of the rare earth magnet ingredient characterized by homogenizing at 700-1250 degrees C before nitriding treatment.

5<=alpha<=181<=beta<=500.1<=gamma<=54<=delta<=30 -- [Claim 12] A component presentation is $R_{\alpha\beta\gamma\delta\epsilon\zeta} \text{Fe}_{100-(\alpha+\beta+\gamma+\delta+\epsilon+\zeta)}$ MbетаBgammaNdeltaHepsilonOzeta. R3 (Fe, M, B)29Ny with the monoclinic system and/or hexagonal crystal structure is included as a main phase. Said R is any one sort of the rare earth elements containing Y, or two sorts or more. Said M aluminum, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, It is the manufacture approach of the rare earth magnet ingredient characterized by consisting of any one sort of Hf, Ta, and the W, or two sorts or more, facing Above alpha, beta, gamma, delta, epsilon, and zeta manufacturing the rare earth magnet ingredient in the range following with atomic percent, and homogenizing at 700-1250 degrees C before nitriding treatment.

5<=alpha<=181<=beta<=500.1<=gamma<=54<=delta<=300.5<=epsilon<=101<=zeta<=5

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the rare earth bond magnet which used a rare earth magnet ingredient, its manufacture approach, and it.

[0002]

[Description of the Prior Art] Although the Nd-Fe-B system magnetic powder which super-quenched as magnetic powder for rare earth bond magnets is conventionally used abundantly, Curie temperature is as low as 300-degree-C order, and since the temperature coefficient (η) of proper coercive force (it is henceforth described as iH_c) is large, the use in an elevated temperature has been restricted. While when Sm_2Fe_{17} compound carries out occlusion of the nitrogen recently shows the Curie temperature of 470 degrees C with no less than 160 degrees C higher than a $Nd_2Fe_{14}B$ compound, being set to 260kOe(s) to which the anisotropy field also far exceeds the anisotropy field (75kOe) of a $Nd_2Fe_{14}B$ compound is reported, and industrialization is considered as magnetic powder for bond magnets. Although nitride $Sm_2Fe_{17}N_x$ of Sm_2Fe_{17} is produced by gas nitriding etc., unless it sets particle size of $Sm_2Fe_{17}N_x$ magnetic powder to about several micrometers, while the high coercive force of 5 or more kOes is not acquired, since the magnetic powder of this particle size oxidizes easily, and that magnet property is degraded and it is accompanied by the danger of the ignition accompanying rapid oxidation, now, it is difficult to put in practical use. Since particle size is several micrometers, in case this $Sm_2Fe_{17}N_x$ magnetic powder is pressed into a bond magnet, it has the problem that a moldability both reduces working efficiency remarkably very bad as if a Plastic solid consistency cannot be raised and the rare earth bond magnet of a high energy product cannot be obtained. Moreover, although it is reported that high coercive force is acquired by the special manufacture approaches, such as the mechanical alloying method, although this approach is suitable for low

production of a laboratory scale, since it is inferior in respect of a cost performance, it has not resulted in mass production. Furthermore, although the $\text{Nd}(\text{Fe}, \text{M})_{12}\text{N}_x$ alloy (M is transition metals, such as V, Ti, Mn, and Mo) with the crystal structure of ThMn_{12} mold, the SmFe_7N_x alloy with the crystal structure of TbCu_7 mold, etc. are examined besides the $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ nitride, it is not inadequate in respect of magnetic properties, or is not put in practical use in the reasons of productivity becoming high cost bad.

[0003] Collocott and others -- the beginning -- Proc. 12th Int. Workshop on RE Magnets and Applications Canberra pp.437- 444 and 1992 (unpublished) It is suggested that $\text{R}_3(\text{Fe}, \text{M})_{29}$ reported alloy is also promising as a permanent magnet ingredient since the nitride $\text{R}_3(\text{Fe}, \text{M})_{29}\text{N}_y$ shows uniaxial magnetic anisotropy. It is Bo-Ping by pulverizing the $\text{Sm}_3(\text{Fe}, \text{Ti})_{29}\text{N}_y$ alloy of this alloy system to the mean particle diameter of 15 micrometers with a ball mill that coercive force is heightened. Hu et al. It is reported by al. (J. Phys.:Condens.Matter 6(1994) L197-L200). However, since the mean diameter is as small as 15 micrometers, this thing is also difficult for lack of a Plastic solid consistency and a moldability putting in practical use as magnetic powder for bond magnets in bad reasons. On the other hand, it is Margarian. et al. It is reported that al. will disassemble $\text{R}_3(\text{Fe}, \text{M})_{29}$ alloy of a J.Appl.Phys.76 (1994) 6135-6155 small lever into other very unstable phases at 900-1000 degrees C. Therefore, this $\text{R}_3(\text{Fe}, \text{M})_{29}$ alloy can be said to be the phase which exists in stability only at an elevated temperature. This is checked also by experiment of this invention persons, and if it adds further, it will be very difficult to obtain the single phase of this $\text{R}_3(\text{Fe}, \text{M})_{29}$ alloy, and will very be easy to generate $\text{R}(\text{Fe}, \text{M})$ alloy and the Fe-M alloy which have the crystal structure of ThMn_{12} mold or $\text{Th}_2\text{Zn}_{17}$ mold.

[0004] Moreover, it is indicated that high coercive force is acquired in the end of coarse powder by introducing N or C using this $\text{R}_3(\text{Fe}, \text{M})_{29}$ alloy in JP,8-111305,A. By using ammonia gas or methane and performing nitriding or carburization processing, after producing $\text{R}_3(\text{Fe}, \text{M})_{29}$ hardener, to the $\text{Sm}_2\text{Fe}_{17}$ above-mentioned compound N, N and C extend the distance between grids of $\text{R}_3(\text{Fe}, \text{M})_{29}$ phase like the time of introducing C, and spontaneous magnetization and Curie temperature increase. That is, installation of N or C is made in order to extend the distance between grids, and this purpose can also attain independent addition of each element. Although how to introduce back N which made the hardener contain C is also considered when using both N and C, in JP,8-111305,A, the role which C is contained in the hardener before nitriding treatment, and is made to stabilize $\text{R}_3(\text{Fe}, \text{M}, \text{C})_{29}$ phase by it, or raises the rate of $\text{R}_3(\text{Fe}, \text{M}, \text{C})_{29}$ phase in a hardener is not played.

[0005]

[Problem(s) to be Solved by the Invention] Since it is necessary to make the temperature coefficient (η) of iH_c small while making the absolute value of iH_c high, in order to improve the thermal resistance of a bond magnet, while an anisotropy field is large, rare earth magnet powder with a high Curie temperature is required. Although the R-Fe-N system alloy is expected as an ingredient with the small temperature coefficient (η) of iH_c since an anisotropy field is larger than the conventional Nd-Fe-B system alloy and Curie temperature is high as mentioned above. For obtaining high iH_c of 5 or more kOes with a R-Fe-N system alloy, it is necessary to make it the shape of several micrometers fines as above-mentioned. It is easy to oxidize, and this impalpable powder is unstable and a moldability is still very worse [impalpable powder] while it cannot fully raise the Plastic solid consistency of a bond magnet in 6 usually used by industrial production - about two 10 ton/cm compacting pressure and cannot gain a high energy product. It is offering the rare earth magnet ingredient which was excellent in thermal stability with the small temperature coefficient (η) of iH_c compared with the former based on the above-mentioned conventional problem while the technical problem of this invention had large iH_c , its manufacture approach, and the rare earth bond magnet using it. Wholeheartedly, as a result of examination, according to this invention, this invention persons are what developed original magnet powder with high anisotropy field and Curie temperature to bond magnets, and it is high iH_c as it is also in the end of coarse powder where particle size is large, and they have the outstanding features that a rare earth magnet ingredient with the small temperature coefficient (η) of iH_c can be offered. That is, completely unlike an operation of above-mentioned C and N, the role of B in this invention dissolves to the main phase, and contributes to stabilization of R₃ (Fe, M, B) 29 phase. Compared with the nitride of the conventional R₃ (Fe, M) 29 main phase, iH_c is size by introducing N into that hardener, and a hardener can be ideally constituted from this phase single phase, while the temperature coefficient (η) of iH_c is smallness, Curie temperature is as high as about 480**20 degrees C, and the rare earth magnet ingredient and rare earth bond magnet of a high energy product can be offered.

[0006]

[Means for Solving the Problem] this invention persons are the purposes which secure the good oxidation resistance of the rare earth magnet powder used for the shaping ease and it in the forming cycle of a bond magnet, and a high magnet property. The result of having considered wholeheartedly the presentation which added the additive to various R-Fe-N system alloys in order that mean particle diameter might obtain high iH_c and high saturation magnetization, and the R-Fe-N system magnet powder which has the

low temperature coefficient (η) of iH_c with coarse powder 20 micrometers or more, It came to accomplish header this invention for the R-Fe-M-B-N system magnet ingredient. Namely, the component presentation of this invention is $R_{\alpha}Fe_{100-(\alpha+\beta+\gamma+\delta)}M_{\beta}B_{\gamma}N_{\delta}$. R3 (Fe, M, B)29Ny with the monoclinic system and/or hexagonal crystal structure is included as a main phase. Said R is any one sort of the rare earth elements including Y, or two sorts or more. Said M consists of any one sort of aluminum, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, and the W, or two sorts or more, and Above α , β , γ , and δ is rare earth magnet ingredients characterized by being in the range following with atomic percent. $5 \leq \alpha \leq 18$, $1 \leq \beta \leq 50$, $1 \leq \gamma \leq 54$, $\delta \leq 30$ [0007] The mixture of two or more sorts of rare earth elements, a misch metal, didym, etc., may be used that what is necessary is just to include any one sort of Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and the Lu, or two sorts or more as the above-mentioned rare earth elements R. As desirable rare earth elements R, it is any one sort of Y, Ce, Pr, Nd, Sm, Gd, Dy, and the Er, or two sorts or more, and is any one sort of Y, Ce, Pr, Nd, and Sm, or two sorts or more still more preferably, and especially a desirable thing is Sm. Here, impurity elements, such as O, H, C, aluminum, Si, Na, Mg, calcium, etc. as which available purity is sufficient and by which mixing on manufacture is not avoided by industrial production, may contain rare earth elements R. The rare earth magnet ingredient of this invention does 5-18 atom % content of R component. Since the deposit of the soft magnetism phase containing many iron components will be promoted, iH_c will fall, if R component becomes under pentatomic %, nonmagnetic R rich compound will deposit and saturation magnetic flux density will be reduced if 18 atom % is exceeded, it is not desirable. Still more desirable R component range is six to 12 atom %.

[0008] As for Fe, it is desirable to contain more than 47 atom %. Fe becomes [saturation magnetization] small and is not desirable at under 47 atom %.

[0009] The above-mentioned M element is effective in raising the decomposition temperature at the time of nitriding so that R3 (Fe, M, B) 29 phase may be later made it stabilized and mentioned under coexistence with B element. Although the additions of M element made to require for generating R3 (Fe, M, B) 29 phase differ for every class of M element, if either of M element is added exceeding 50 atom %, the yield of R(Fe, M, B)12 phase which has the crystal structure of $ThMn_{12}$ mold will become large, and iH_c will fall rapidly. The yield of R2 (Fe, M, B) 17 phase in which M element has the crystal structure of Th_2Zn_{17} mold under by 1 atom % becomes large, the rate of an abundance ratio of R3 (Fe, M, B) 29 phase falls relatively, and neither has it. [desirable] Therefore, the desirable addition of M element is one to 50 atom %. An element desirable among M

elements is any one sort of Ti, Mn, Cr, Zr, and the V, or two sorts or more. Although M element is indispensable for generating R3 (Fe, M, B) 29 phase, R3 (Fe, M) 29 phase which does not contain B is unstable as above-mentioned, and since it is easy to decompose into other phases at the time of homogenization or nitriding treatment, it is very difficult [it] to obtain the rare earth magnet powder of R3 (Fe, M)29Ny phase single phase.

[0010] Since the generation ratio of nitride R3 (Fe, M)29Ny is low even if it will nitride, if the rate of R3 (Fe, M) 29 phase in the hardener with which nitriding is presented is low, a good magnet property cannot be acquired. In consideration of this point, this invention persons found out that R3 (Fe, M, B) 29 desirable stable phase near the single phase more than 75 volume % was obtained more than 60 volume %, when Above B and M element lived together. Therefore, in the hardener before nitriding treatment, the abundance of R3 (Fe, M, B) 29 phase can be raised by leaps and bounds. since it is markedly alike and increases compared with the case where R3 (Fe, M) 29 phase in which the abundance of the R3 (Fe, M, B)29Ny phase occupied in the rare earth magnet ingredient after nitriding treatment does not contain the conventional B is nitrified, it becomes possible high flux density and to generate high coercive force. In this invention, the desirable content of B is 0.1 - pentatomic %. Since an R3 (Fe, M, B)29Ny nitride phase will become unstable and it will become easy to decompose to other phases if B exceeds under 0.1 atom % and pentatomic %, it is not desirable. That is, the operation which stabilizes R3 (Fe, M, B) 29 phase is demonstrated when it is in the range of the above-mentioned B addition. The effectiveness by B addition of such a minute amount is not known until now. for example, about the solid-solution limit when adding B, C, and N to Sm2Fe17 alloy H. Horiuchi et According to the report of al (J. Alloys.Comp.222 (1995) 131-135), C About 7 atoms %, B dissolves only to about 1 atom % to N dissolving to about 14 atoms %, but the flare of the grid by dissolution of B and the rise of Curie temperature are made very small. These considered each of C, N, and B as an element of an invasion mold, and aimed at the escape of the distance between grids by installation of these elements, and the technique of attaining stabilization of the above-mentioned main phase by B addition of a minute amount like this invention was not found out until now. The coexistence effectiveness of B and M element in this invention raises the abundance of R3 (Fe, M, B) 29 phase in a hardener as above-mentioned, and has the effectiveness which controls the decomposition to other phases, such as α Fe, in homogenization or nitriding treatment. For example, in the former, the range is [whenever / stoving temperature / with R3 (Fe, M) 29 stable phase] narrow in homogenization. Moreover, the nitriding phase once generated when the case

where nitriding temperature is high, and long duration nitriding were performed : although R3 (Fe, M)29Ny is unstable and the coercive force of the magnet ingredient with which αFe etc. might be generated declines greatly In the case of this invention, the range of large homogenization temperature and nitriding temperature is employable by carrying out optimum dose addition of the B, and it is effective also in stabilization of improvement in productivity, and the magnet quality of a rare earth magnet ingredient. Furthermore, since M element can be reduced conventionally, it also has the effectiveness that saturation magnetic flux density (residual magnetic flux density), i.e., an energy product, increases, at the same time it spreads compared with the case where the content range of M element contributed to stabilization of R3 (Fe, M, B) 29 phase is R3 (Fe, M) 29 conventional phase, by B addition.

[0011] As for the nitrogen N introduced into R3 (Fe, M, B) 29 phase, it is desirable to consider as four to 30 atom %. It is difficult to raise coercive force under by 4 atom %, if magnetization exceeds 30 atom % while Nitrogen N becomes low. The content of more desirable nitrogen N is ten to 20 atom %.

[0012] Moreover, while it is desirable to permute 0.01 - 30 atom % of Fe with Co and/or nickel and Curie temperature rises by installation of Co and/or nickel, it is effective in the temperature coefficient (η) of iH_c and oxidation resistance improving. The more desirable range of the amount of Fe permutations by Co and/or nickel is one to 20 atom %. If the amount of permutations exceeds 30 atom %, while inviting saturation magnetic flux density and the remarkable fall of iH_c , the addition effectiveness of Co and/or nickel is not accepted under by 1 atom %.

[0013] By setting 70% or more to Sm preferably more than 50 atom % of R component of this invention, since it is conspicuous and high iH_c is obtained, it is desirable. Moreover, it is desirable to set mean particle diameter of the rare earth magnet ingredient of this invention to 20-500 micrometers. It produces the fault by which a nitride is not formed in a powder particle at homogeneity that the diffusion length of nitrogen tends to become inadequate to a powder particle with big particle diameter on the usual nitriding conditions and is not desirable, if quality degradation and moldability degradation by oxidation become remarkable and exceed 500 micrometers in less than 20 micrometers. The range of more desirable mean particle diameter is 30-400 micrometers. Moreover, when it has the organization where M element or M compound deposited in the crystal grain of an R3 (Fe, M, B)29Ny phase, the temperature coefficient (η) of high iH_c and low iH_c can be obtained.

[0014] moreover, the rate of an abundance ratio of the R3 (Fe, M, B)29Ny phase [according to this invention] in a rare earth magnet ingredient -- 60 volume % -- the

thing of 75 volume % can be offered easily preferably.

[0015] Moreover, this invention is a rare earth magnet ingredient with which it is combined by a giant-molecule polymer, a pure metal, or the alloy, and the magnet powder constitutes a bond magnet, and it is a rare earth magnet ingredient characterized by the proper coercive force (iHc) in 25 degrees C being 8 or more kOes while the temperature coefficient (eta) of the proper coercive force (iHc) in 25-100 degrees C of said magnet powder is -0.45 or more.

[0016] Moreover, the component presentation of this invention is $R\alpha Fe_{100-(\alpha+\beta+\gamma+\delta+\epsilon+\zeta)}$

$M\beta B\gamma N\delta H\epsilon O\zeta$. R3 (Fe, M, B)29Ny with the monoclinic system and/or hexagonal crystal structure is included as a main phase. Said R is any one sort of the rare-earth elements containing Y, or two sorts or more. Said M consists of any one sort of aluminum, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, and the W, or two sorts or more, and Above alpha, beta, gamma, delta, epsilon, and zeta is rare earth magnet ingredients characterized by being in the range following with atomic percent.

1- pentatomic % By adjusting performing hydrogen processing at a process until it presents nitriding, and grinding grain size, the rare earth magnet ingredient of $5 \leq \alpha \leq 181 \leq \beta \leq 500.1 \leq \gamma \leq 54 \leq \delta \leq 300.5 \leq \epsilon \leq 101 \leq \zeta \leq 5$ this invention can include 0.5 to 10 atom %, and/or Oxygen O for Hydrogen H in the last nitriding magnetism powder. When hydrogen is 0.5-10 atom % Included, it is effective in raising the effectiveness of nitriding. This is considered because nitrogen can be spread in R3 (Fe, M, B) 29 phase in a short time in order that nitrogen may replace the hydrogen which has already existed in R3 (Fe, M, B) 29 phase. However, since the hydrogen diffused while saturation magnetization decreased will serve as a surplus if the effectiveness is not accepted under by 0.5 atom % but hydrogen exceeds 10 atom %, it will become unstable chemically. Next, when 1- pentatomic % content of oxygen is done, the effectiveness which enlarges the temperature coefficient (eta) of iHc is accepted. Since magnetization and the fall of iHc will become remarkable if the effectiveness is not accepted under by 1 atom % but oxygen exceeds pentatomic %, it is not desirable.

[0017] Moreover, while this invention is the rare earth bond magnet which combined the above-mentioned magnet powder with features with one binder of a giant-molecule polymer, a pure metal, and an alloy and the temperature coefficient (eta) of the proper coercive force (iHc) in 25-100 degrees C of said rare earth bond magnet is -0.45 or more, it is the rare earth bond magnet with which coercive force (bHc) in 25 degrees C is characterized by being 6 or more kOes.

[0018] Moreover, the component presentation of this invention is $R\alpha Fe_{100-(\alpha+\beta+\gamma+\delta)} M\beta B\gamma N\delta$. R3 (Fe, M, B)29Ny with the monoclinic system and/or hexagonal crystal structure is included as a main phase. Said R is any one sort of the rare earth elements including Y, or two sorts or more. Said M consists of any one sort of aluminum, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, and the W, or two sorts or more, and Above alpha, beta, gamma, and delta is faced manufacturing the rare earth magnet ingredient in the range following with atomic percent. It is the manufacture approach of the rare earth magnet ingredient characterized by homogenizing at 700-1250 degrees C before nitriding treatment.

5<= α <=181<= β <=500.1<= γ <=54<= δ <=30 [0019] Moreover, the component presentation of this invention is $R\alpha Fe_{100-(\alpha+\beta+\gamma+\delta+\epsilon+\zeta)} M\beta B\gamma N\delta H\epsilon O\zeta$.

R3 (Fe, M, B)29Ny with the monoclinic system and/or hexagonal crystal structure is included as a main phase. Said R is any one sort of the rare earth elements containing Y, or two sorts or more. Said M aluminum, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, It is the manufacture approach of the rare earth magnet ingredient characterized by consisting of any one sort of Hf, Ta, and the W, or two sorts or more, facing Above alpha, beta, gamma, delta, epsilon, and zeta manufacturing the rare earth magnet ingredient in the range following with atomic percent, and homogenizing at 700-1250 degrees C before nitriding treatment.

[0020]

[Embodiment of the Invention] This invention is explained in full detail below. Although the rare earth magnet ingredient of this invention has the ideal thing of the single phase of an R3 (Fe, M, B)29Ny phase which has the monoclinic system and/or hexagonal crystal structure, other compounds (it is henceforth called a subphase) which are not contributed to the magnet property other than this main phase can be contained. Although the R-Fe-M-B-N system magnetism compound which has the crystal structure of Th₂Zn₁₇ mold, TbCu₇ mold, ThMn₁₂ mold, etc. as this subphase may be included, as above-mentioned, more than 60 volume % of the content ratio of the main phase of this invention is desirable, and more than its 75 volume % is more desirable. Although the R3 (Fe, M, B)29Ny main phase is obtained when nitrogen invades between the crystal lattices of R3 (Fe, M, B) 29 phase which mainly constitutes all hardeners or a hardener and the crystal lattice expands, the crystal structure has the almost same symmetric property as R3 (Fe, M, B) 29 phase. For example, when the thing of a presentation of Sm_{9.4}Fe_{84.0} B-2.0Ti_{4.5} is chosen by atomic % display as hardener powder, by introducing nitrogen, a crystal magnetic anisotropy changes from plane anisotropy to

uniaxial anisotropy, and will become suitable as a permanent magnet ingredient.

[0021] Although the rare earth bond magnet concerning this invention comes to harden the above-mentioned rare earth magnet ingredient with the binder of a giant-molecule polymer, a pure metal, or an alloy, well-known things, such as thermoplastics, such as the heat-curing resin or polyamide resin represented by an epoxy resin, phenol resin, etc. as a giant-molecule polymer, and EEA resin, or synthetic rubber, and natural rubber, can be used for it. Moreover, as a pure metal or an alloy, well-known low-melt point metals and low melting alloys, such as zinc and tin, can be used. Moreover, as the shaping approach of a rare earth bond magnet, the well-known shaping approaches, such as compression molding and injection molding, are employable.

[0022] Since a rare earth magnet ingredient with the high rate of an abundance ratio of the R₃ (Fe, M, B)₂₉Ny main phase is producible to easy and stability according to this invention While Curie temperature is highly excellent in thermal stability with about 480**20 degrees C and rare earth magnet powder with the temperature coefficient (eta) of iHc with high abbreviation regularity and low iHc can be offered covering a broad particle size of 20-500 micrometers with mean particle diameter The isotropy of a high magnet property and an anisotropy bond magnet can be manufactured easily.

[0023] Next, the typical production process of this invention is explained.

[0024] (Adjustment of a hardener) The magnet ingredient of this invention raises the content ratio of R₃ (Fe, M, B) ₂₉ phase in the R-Fe-M-B system hardener with which nitriding treatment is presented by compound addition with B and M element. A R-Fe-M-B system hardener is alloyed using for example, a RF solution process, an arc solution process, a super-quenching method, the strip cast method, the gas atomizing method, a reduction diffusion method, or the mechanical alloying method. Heating maintenance of the alloy obtained by the above-mentioned approach is carried out under a hydrogen ambient atmosphere, dehydrogenation treatment may be performed continuously, a hydride may be made to decompose, and you may make it recombine with a hardener phase. When a RF solution process or an arc solution process is used, in case the above-mentioned alloy solidifies here, the soft magnetism phase which uses alphaFe as a principal component tends to deposit, but since this soft magnetism phase becomes the factor which after nitriding treatment remains and reduces coercive force, it is not desirable. For suppressing generation of this soft magnetism phase, it is desirable to homogenize the ingoted hardener by the inside of a vacuum or the argon gas ambient atmosphere on the heating conditions of 700-1250 degree·Cx 0.5 · 100 hours. R₃ (Fe, M) ₂₉ conventional phase has the advantage which can permit the large homogenization temperature of 700-1250 degrees C by this invention to decomposing at

900-1000 degrees C as above-mentioned.

[0025] (Grinding) Although it is also possible to nitride directly the hardener lump which ingoted by the above-mentioned approach, or the thing which carried out mechanical alloying, since nitriding treatment time amount will become long if the size of a nitriding treatment object is large, it is desirable to perform coarse grinding and to nitride after coarse grinding to 500 micrometers or less with mean particle diameter. Coarse grinding can be performed using grinders, such as a disc mill, a bantamweight division mill, a jaw crusher, and a ball mill. Moreover, after carrying out occlusion of the hydrogen to a hardener, the approach of carrying out coarse grinding with the above-mentioned grinder and the approach of repeating and carrying out coarse grinding of the occlusion of hydrogen and the emission may be used. After coarse grinding, since the main phase of a homogeneous nitride can be formed into a hardener if it classifies and nitrifies by the screen, are still more desirable. Before nitriding treatment, for example, 20 micrometers - less than 100 micrometers, 100 micrometers - less than 200 micrometers, If screen analysis is carried out like 200 micrometers - less than 300 micrometers, 300 micrometers - less than 400 micrometers, and 400 micrometers - less than 500 micrometers, the magnet powder after nitriding treatment will have such screen analysis particle size mostly. Since the magnet powder of such abbreviation screen analysis particle size is employable suitably according to the difficulty of the moldability demanded according to a bond magnet configuration with the above-mentioned homogeneous nitridation effectiveness, it is suitable practically. Furthermore, after coarse grinding, although a magnet property will improve if it anneals in an argon gas ambient atmosphere or a vacuum in 500-1000 degree-Cx 0.5 - 100 hours, this effectiveness is considered because distortion introduced by coarse grinding is eased.

[0026] (Nitriding) The well-known nitriding treatment approach can be adopted in this invention (for example, gas nitriding, ion nitriding, etc.). Gas nitriding is explained as an example. Gas nitriding is a process which either, such as mixed gas of nitrogen gas, ammonia gas, nitrogen gas, the mixed gas of hydrogen gas and ammonia gas, and hydrogen gas, is contacted into the coarse-grinding powder of the above-mentioned hardener lump or the above-mentioned hardener, and introduces nitrogen in a crystal lattice. A nitriding reaction is [whenever / choosing-above types of gas and stoving temperature] controllable by heating time and gas pressure. Among these, whenever [stoving temperature] has desirable 300-650 degrees C, although it changes with hardener presentations. Since the once generated nitride will decompose and soft magnetism phases, such as αFe , will generate if it is not based on the class of

hardener, and nitriding hardly advances that it is less than 300 degrees C and it exceeds 650 degrees C, it is not desirable. If it anneals in inert gas, such as an argon, a vacuum, or hydrogen gas further after nitriding for 300-600 degree-Cx 0.5 to 50 hours, coercive force, iH_c , saturation magnetization, etc. may improve. This is considered for forming a nitride in homogeneity and going in that nitrogen is further spread in the crystal grain child of a hardener by annealing, and the rate of the nitride phase of the main phase increases, or a powder particle.

[0027] (Magnetic field shaping) In order to produce an anisotropy bond magnet using the rare earth magnet ingredient powder of this invention created as mentioned above After mixing the binder of the magnet powder and thermosetting resin, or a low-melt point point metal (low melting alloys) by the proper ratio, press all over the magnetic field of 10 or more kOes, or The approach of carrying out injection molding of the compound which blended, carried out heating kneading and obtained the magnet powder and thermoplastics by the proper ratio all over the magnetic field of 10 or more kOes is employable. What is necessary is to form a Plastic solid without a magnetic field and just to perform the afterbaking hardening processing, after mixing the rare earth magnet ingredient powder of this invention for equalization after combination by the binder powder and proper ratio of the above-mentioned resin or a metal (alloy), in producing an isotropic bond magnet.

[0028] (Magnetization) 15 or more kOes of things performed more preferably in the magnetization magnetic field of 20 or more kOes of the magnetization activity for giving sufficient magnetism for the above-mentioned bond magnet are preferably common.

[0029] Next, the evaluation approach of each physical-properties value of this invention is explained concretely.

(Measurement of mean particle diameter) The mean particle diameter of the above-mentioned magnet ingredient powder measured the volume nominal diameter distribution using the laser diffraction type particle-size-distribution measuring device (the product made from GALAI, CIS-1 mold), and asked for mean particle diameter from the distribution curve.

(Measurement of magnetic properties) iH_c of the above-mentioned magnet ingredient and saturation magnetization (σ) mixed the specified quantity of the magnet powder with resin, stuffed it into the copper container, and were measured using the oscillating sample mold magnetometer (Toei Industry VSM-3 mold). iH_c of a bond magnet, the residual magnetic flux density (B_r), and the temperature coefficient (η) of iH_c were measured using the account fluxmeter of ** (Toei Industry TRF- 5 H).

[0030] (Component analysis) Nitrogen, hydrogen, and oxygen were analyzed by the

gas-chromatography heat-conduction detecting method among the configuration elements of the above-mentioned magnet ingredient using N, O, and H gas analyser (EMGA1300 by Horiba, Ltd.). Moreover, M elements, such as 2 potassium-chromate volumetric method and Ti, and B analyzed rare earth elements, such as Sm, with the oxalate weight method, and Fe analyzed them by the inductive-coupling mold plasma-emission-spectrometry method.

[0031] (Oxidation-resistant evaluation) After leaving rare earth magnet powder for 168 hours in the thermostat held in atmospheric air at 90% of 100 degree-Cx relative humidity, it took out, iHc was measured at 25 degrees C, and the oxidation resistance which is percentage reduction was searched for as compared with iHc in 25 degrees C before putting into this thermostat. Namely,
$$\text{Oxidation resistance} = \frac{\text{iHc in 25 degrees C of magnet powder after thermostat processing}}{\text{iHc in 25 degrees C of magnet powder before thermostat processing}} \times 100 (\%)$$
 It is the defined value. It excels in oxidation resistance, so that this value is small.

[0032] Next, this invention is not limited by these although an example explains this invention.

(Examples 1-12) In order to see correlation with B addition and a magnet property, the rare earth magnet powder shown in Table 1 was produced and evaluated. First, it blended respectively so that it might become the hardener presentation corresponding to the nitride magnet powder of the examples 1-12 of Table 1 using Sm, Fe, Ti, and B of 99.9% of purity, and it dissolved with the RF fusion furnace of an argon gas ambient atmosphere, and each hardener corresponding to examples 1-12 was ingoted. Then, this hardener lump was continuously performed 1150 degrees C and homogenization of 20 hours and ground using the jaw crusher and the disc mill in the argon gas ambient atmosphere. When the X diffraction of these hardener fine particles was performed using Cu-K alpha rays, it checked that all diffraction lines could carry out indexing as R3 (Fe, M, B) 29 phase. Next, each above-mentioned hardener powder was taught to the ambient atmosphere heating furnace, heating maintenance was carried out in the nitrogen gas 1atm air current in 450 degrees C for 5 hours, and nitriding treatment was performed, and it annealed at 420 degrees C in the argon air current continuously for 1 hour. When the X diffraction of each of these fine particles that carried out nitriding treatment was performed, it had shifted to a side whenever [low angle-of-diffraction] and N atom invaded into a hardener crystal from the X diffraction pattern of R3 (Fe, M, B) 29 phase obtained with the hardener, it has checked that that crystal lattice had spread. In this way, the result of having reached in the strength of the presentation of the nitride magnet powder of the acquired examples 1-12, mean particle diameter, and

the saturation magnetization in 25 degrees C (σ), and having measured the temperature coefficient (η) of iH_c and iH_c in 25-100 degrees C was shown in Table 1. Here, the whole of each measurement in following each example and each example of a comparison is performed on measurement and these conditions of Table 1.

[0033] (Examples 1-6 of a comparison) As shown in Table 1, while considering as the hardener presentation which does not contain B, the nitride magnet powder of the examples 1-6 of a comparison shown in Table 1 like an example 1 was produced and evaluated except having changed mean particle diameter. Generation of $Sm_2(Fe, Ti, B)_{17}$ phase of Th_2Zn_{17} mold, αFe , and/or a Fe-Ti phase was accepted in the hardener powder before the nitriding treatment of these examples 1-6 of a comparison that do not contain B.

[0034]

[Table 1]

	稀土類磁石粉末組成 (原子%)	平均粒径 (μm)	σ (emu/g)	iHc (kOe)	η (%/°C)
実施例 1	Sm8.2FeBa1B2.0Ti4.0N12.7	20	129	8.1	-0.37
実施例 2	Sm8.2FeBa1B2.0Ti4.1N12.9	40	133	11.5	-0.35
実施例 3	Sm8.4FeBa1B2.0Ti4.2N12.5	70	132	12.9	-0.34
実施例 4	Sm8.3FeBa1B2.0Ti4.1N12.7	140	132	12.3	-0.33
実施例 5	Sm8.2FeBa1B2.0Ti4.0N12.3	260	130	11.9	-0.33
実施例 6	Sm8.3FeBa1B2.0Ti4.2N12.4	420	128	11.3	-0.32
実施例 7	Sm8.3FeBa1B2.0Ti4.2N12.4	500	131	8.0	-0.32
実施例 8	Sm8.3FeBa1B0.1Ti4.2N12.4	140	129	8.4	-0.39
実施例 9	Sm8.3FeBa1B0.5Ti4.2N12.4	140	136	11.2	-0.38
実施例 10	Sm8.3FeBa1B1.0Ti4.2N12.4	140	134	9.7	-0.32
実施例 11	Sm8.3FeBa1B3.0Ti4.2N12.4	140	130	10.3	-0.39
実施例 12	Sm8.3FeBa1B5.0Ti4.2N12.4	140	126	9.1	-0.39
比較例 1	Sm8.3FeBa1Ti4.2N12.7	20	132	2.9	-0.59
比較例 2	Sm8.3FeBa1Ti4.2N12.5	85	130	2.1	-0.57
比較例 3	Sm8.3FeBa1Ti4.2N12.2	240	127	1.8	-0.55
比較例 4	Sm8.2FeBa1Ti4.1N12.5	490	125	1.9	-0.54
比較例 5	Sm8.3FeBa1B0.05Ti4.2N12.4	130	130	2.1	-0.55
比較例 6	Sm8.3FeBa1B6.0Ti4.2N12.4	130	119	1.5	-0.53

[0035] The effectiveness of compound addition of B and M element is clearer than Table 1. That is, in the examples 1-12 0.1- pentatomic % Containing B, while high iHc of 8 or more kOes is obtained covering the mean particle diameter of 20-500 micrometers, the temperature coefficient (η) of iHc is also known by having good thermal resistance or more by -0.45. On the other hand, it turns out that iHc is -0.53 or less and each thing of the example of a comparison which does not contain B is inferior to thermal resistance also in the temperature coefficient (η) of iHc by less than 3 kOes.

[0036] (Examples 13-15) In order to see correlation with R quantitative formula, and the class of R component and a magnet property, while manufacturing the magnet powder shown in Table 2 by the same actuation as the above-mentioned example 1, saturation magnetization (σ) and the temperature coefficient (η) of iHc and iHc were

measured except having considered as the mean particle diameter of 72 micrometers, while making it the magnet powder presentation shown in Table 2.

(Examples 7-10 of a comparison) Except having made it the magnet powder presentation shown in Table 2, while manufacturing the magnet powder shown in Table 2 like examples 13-15, saturation magnetization (σ) and the temperature coefficient (η) of iH_c and iH_c were measured.

[0037]

[Table 2]

	希土類磁石粉末組成 (原子%)	σ (emu/g)	iH_c (kOe)	η (%/°C)
実施例 13	Sm8.3FeBaB2.0Ti4.0N12.1	130	8.5	-0.35
実施例 14	Sm6.2Pr2.0FeBaB2.0Ti4.0N12.3	125	8.8	-0.37
実施例 15	Sm5.2Pr3.1FeBaB2.0Ti4.1N12.9	122	8.1	-0.35
比較例 7	Sm3.9Pr4.4FeBaB2.0Ti4.1N12.9	125	2.8	-0.63
比較例 8	Sm2.2Pr6.1FeBaB2.0Ti4.1N12.9	120	1.9	-0.64
比較例 9	Sm3.2FeBaB2.0Ti4.0N10.3	136	2.5	-0.59
比較例 10	Sm19.3FeBaB2.0Ti4.2N12.4	89	3.1	-0.54

[0038] Table 2 shows that the temperature coefficient (η) of iH_c high when Sm ratio in R component is more than 50 atom %, and low iH_c is obtained.

[0039] (Examples 16-20) In order to see correlation with R quantitative formula, and the class of R component and a magnet property following the above-mentioned table 2, while obtaining the magnet powder shown in Table 3 by the same actuation as the above-mentioned example 1, the temperature coefficient (η) of magnetization, and iH_c and iH_c was measured except having changed mean particle diameter into 130 micrometers, while making it the magnet powder presentation shown in Table 3.

(Examples 11-14 of a comparison) The same evaluation as examples 16-20 was performed except having considered as the magnet powder presentation of Table 3.

[0040]

[Table 3]

	希土類磁石粉末組成 (原子%)	σ (emu/g)	iHc (kOe)	η (%/°C)
実施例 16	Sm5.0Fe bal B2.0Ti4.0N12.1	136	8.2	-0.39
実施例 17	Sm8.3Fe bal B2.0Ti4.0N12.1	132	12.3	-0.35
実施例 18	Sm6.2Pr2.0Fe bal B2.0Ti4.0N12.3	125	10.8	-0.37
実施例 19	Sm5.2Pr3.1Fe bal B2.0Ti4.1N12.9	122	9.1	-0.36
実施例 20	Sm14.9Pr3.1Fe bal B2.0Ti4.1N12.9	92	10.5	-0.38
比較例 11	Sm4.8Fe bal B2.0Ti4.0N10.3	126	3.5	-0.31
比較例 12	Sm19.3Fe bal B2.0Ti4.2N12.4	105	2.1	-0.59
比較例 13	Sm3.2Pr1.6Fe bal B2.0Ti4.0N11.3	126	3.5	-0.50
比較例 14	Sm15.5Pr3.5Fe bal B2.0Ti4.2N12.4	95	3.9	-0.59

[0041] Table 3 shows that the temperature coefficient (η) of iHc high when Sm ratio in R component is more than 50 atom % and R component is five to 18 atom %, and low iHc is obtained.

[0042] (Examples 21-24) In order to see correlation with a nitrogen content and a magnet property, while obtaining the magnet powder of Table 4 like the above-mentioned example 1, saturation magnetization (σ) and the temperature coefficient (η) of iHc and iHc were measured except having set to 120 micrometers the magnet powder presentation and mean particle diameter which are shown in Table 4. (Examples 15 and 16 of a comparison) The same evaluation as examples 21-24 was performed except having considered as the magnet powder presentation of Table 4.

[0043]

[Table 4]

	希土類磁石粉末組成 (原子%)	σ (emu/g)	iHc (kOe)	η (%/°C)
実施例 2 1	Sm8.3FeBa1B2.0Ti4.0N4.0	122	9.3	-0.39
実施例 2 2	Sm8.3FeBa1B2.0Ti4.0N15.3	131	10.8	-0.37
実施例 2 3	Sm8.1FeBa1B2.0Ti4.1N20.9	138	14.1	-0.38
実施例 2 4	Sm8.2FeBa1B2.0Ti4.1N30.0	119	9.8	-0.39
比較例 1 5	Sm8.2FeBa1B2.0Ti4.1N3.5	92	2.9	-0.49
比較例 1 6	Sm8.2FeBa1B2.0Ti4.0N32.1	106	2.5	-0.51

[0044] Table 4 shows that the temperature coefficient (η) of high iHc and low iHc is obtained in the examples 21-24 in which 4-30 atom % content of nitrogen volume was done. As shown in the examples 15 and 16 of a comparison, the time with less nitrogen volume than pentatomic %, and when [than 30 atom %] more, iHc is the value of less than 3 kOes low.

[0045] (Examples 25-29) In order to see a magnet property when Co or nickel permutes Fe component, while obtaining the magnet powder of Table 5, saturation magnetization (σ) and the temperature coefficient (η) of iHc and iHc were measured by the same actuation as the above-mentioned example 1 except having set mean particle diameter to 170 micrometers, while changing into the magnet powder presentation shown in Table 5.

(Examples 17-19 of a comparison) The same evaluation as examples 25-29 was performed except having considered as the magnet powder presentation of Table 5.

[0046]

[Table 5]

	希土類磁石粉末組成 (原子%)	σ (emu/g)	iHc (kOe)	η (%/°C)	耐酸化 性(%)
実施例25	Sm8.3FeBaCo0.01B2.0Ti4.0N12.1	130	8.3	-0.32	-1.8
実施例26	Sm8.3FeBaCo1.0B2.0Ti4.0N12.3	128	8.2	-0.30	-0.9
実施例27	Sm8.2FeBaCo30.0B2.0Ti4.1N12.9	94	8.1	-0.30	-0.1
実施例28	Sm8.3FeBaNi1.0B2.0Ti4.0N10.3	110	8.5	-0.31	-1.2
実施例29	Sm8.3FeBaCo20.0Ni10.0B2.0Ti4.0 N10.3	106	8.5	-0.31	-1.1
比較例17	Sm8.3FeBaB2.0Ti4.0N12.1	129	8.2	-0.39	-2.5
比較例18	Sm8.1FeBaCo0.005B2.0Ti4.1N12.9	131	8.2	-0.37	-2.4
比較例19	Sm8.2FeBaCo33.0B2.0Ti4.1N12.9	92	3.9	-0.52	-0.1

[0047] When Co and/or nickel permute a part of Fe in the range of 0.01 - 30 atom % from Table 5, while oxidation resistance improves, it turns out that the temperature coefficient (η) of high iHc and low iHc is obtained.

[0048] (Examples 30-36) The amount of H and the amount of O which are contained to the magnet powder of each above-mentioned example were unescapable impurity extent, for example, H content was [50 ppm or less and O content] 5000 ppm or less in the weight % display. However, the magnet powder of this invention can contain H and O exceeding an unescapable impurity content by choosing manufacture conditions suitably as above-mentioned. In order to see the effect by the amount of H and the amount of O which were made to contain positively, while manufacturing the magnet powder of the presentation shown in Table 6, except having set mean particle diameter to 400 micrometers, by the same actuation as the above-mentioned example 1, the magnet powder of Table 6 was obtained and saturation magnetization (σ) and the temperature coefficient (η) of iHc and iHc were measured.

(Examples 20-24 of a comparison) It evaluated like examples 30-36 except having considered as the magnet powder presentation of Table 6.

[0049]

[Table 6]

	希土類磁石粉末組成 (原子%)	σ (emu/g)	i Hc (KOe)	η (%/°C)
実施例 3 0	Sm8.3FeBa1B2.0Ti4.0N12.1H0.5	130	8.3	-0.31
実施例 3 1	Sm8.3FeBa1B2.0Ti4.0N12.1H5.1	128	9.2	-0.33
実施例 3 2	Sm8.3FeBa1B2.0Ti4.0N12.1H10.0	103	9.5	-0.34
実施例 3 3	Sm8.3FeBa1B2.0Ti4.0N12.1O1.0	125	8.6	-0.32
実施例 3 4	Sm8.3FeBa1B2.0Ti4.0N12.1O3.0	118	8.3	-0.31
実施例 3 5	Sm8.3FeBa1B2.0Ti4.0N12.1O5.0	102	8.8	-0.30
実施例 3 6	Sm8.3FeBa1B2.0Ti4.0N12.1H0.5O1.0	128	8.5	-0.32
比較例 2 0	Sm8.3FeBa1B2.0Ti4.0N12.1H0.4	130	8.5	-0.37
比較例 2 1	Sm8.3FeBa1B2.0Ti4.0N12.1H12.0	125	8.6	-0.49
比較例 2 2	Sm8.3FeBa1B2.0Ti4.0N12.1O0.5	129	8.5	-0.37
比較例 2 3	Sm8.3FeBa1B2.0Ti4.0N12.1O7.0	94	3.0	-0.49
比較例 2 4	Sm8.3FeBa1B2.0Ti4.0N12.1H12.0O7.0	90	2.9	-0.48

[0050] When 0.5 to 10 atom % and/or oxygen have hydrogen in 1 - pentatomic % from Table 6, it turns out that high iHc and high saturation magnetization (σ), and a low temperature coefficient (η) are obtained. Moreover, especially in the thing of each example of a comparison by which 0.5 to 10 atom % and/or oxygen separated [the amount of hydrogen] from the range of 1 - pentatomic %, it turns out that the temperature coefficient (η) has deteriorated.

[0051] (Examples 37-44) In order to see the effect to the class of M element, and the magnet property of a content, while making it the magnet powder presentation shown in Table 7, except having set mean particle diameter to 170 micrometers, by the same actuation as the above-mentioned example 1, the magnet powder of Table 7 was obtained and saturation magnetization (σ) and the temperature coefficient (η) of iHc and iHc were measured.

(Examples 25 and 26 of a comparison) The same evaluation as examples 37-44 was performed except having considered as the magnet powder of Table 7.

[0052]

[Table 7]

	希土類磁石粉末組成 (原子%)	σ (emu/g)	i Hc (KOe)	η (%/°C)
実施例 3 7	Sm8.3Fe bal B2.0Ti 1.0N12.1	132	8.3	-0.37
実施例 3 8	Sm8.3Fe bal B2.0Ti 8.0N12.1	112	9.7	-0.36
比較例 2 5	Sm8.1Fe bal B2.0Ti 0.5N9.9	122	3.1	-0.51
実施例 3 9	Sm8.2Fe bal B2.0Mn 20.2N12.9	119	10.1	-0.38
実施例 4 0	Sm8.2Fe bal B2.0Mn 50.0N12.9	92	8.1	-0.42
比較例 2 6	Sm8.2Fe bal B2.0Mn 60.0N13.9	72	3.1	-0.50
実施例 4 1	Sm8.3Fe bal B2.0V10.1N11.9	120	11.9	-0.33
実施例 4 2	Sm8.2Fe bal B2.0Al 4.0N10.3	126	12.5	-0.36
実施例 4 3	Sm8.3Fe bal B2.0Ti 4.2Zr 8.2N13.4	119	12.1	-0.34
実施例 4 4	Sm8.3Fe bal B2.0Cr 3.6Nb 7.2N10.4	125	10.1	-0.39

[0053] Table 7 shows that the temperature coefficient (η) of iHc high when M element is one to 50 atom %, and low iHc is obtained. As shown in the examples 24 and 25 of a comparison, when there was no M element in this range, it turned out that iHc does not improve even if Sm₃(Fe, M, B)₂₉ phase does not carry out little deer generation but nitrides in a hardener.

[0054] (Example 45) The hardener corresponding to the following magnet powder presentation which added Cr as an M element and permuted a part of Fe by Co was carried out after the ingot, coarse grinding of the hardener was carried out in the one mol % [of oxygen tension] nitrogen air current on the same dissolution conditions as the above-mentioned example 1, and the sieve adjusted to the average grain size of 125 micrometers. This Sm-Fe-Co-B-Cr system alloy powder was annealed in the argon air current of oxygen tension 10⁻⁵atm for 1 hour, after performing nitriding treatment of 5 hours at 460 degrees C in the ammonia-hydrogen mixed-gas air current of ammonia partial pressure 0.35atm and hydrogen partial-pressure-of-gas 0.65atm. The ball milling of Sm_{9.4}Fe_{64.1}Co_{4.0}B_{1.0}Cr_{4.5}N_{16.5}H_{0.5} [with a mean particle diameter of 74 micrometers obtained] was carried out for 30 minutes in the cyclohexane. The mean particle diameter of the presentation of this pulverized powder was 36 micrometers in Sm_{9.2}Fe_{64.0}Co_{4.0}B_{1.0}Cr_{4.5}N_{16.0}H_{0.5}O_{1.0} at atomic % display. this magnetic powder -- iHc -- 8 -- the temperature coefficient (η) of kOe(s) and iHc was a good value of

-0.31%/degree C.

[0055] (Example 46) The piece of thin film integrated circuit casting of about 2mm of board thickness was obtained using the congruence roll type strip axle-pin rake who installed the two copper roll with a diameter of 300mm for the alloy molten metal dissolved with the RF fusion furnace under an argon gas ambient atmosphere after blending with the hardener presentation corresponding to the following nitride powder using Sm, Fe, Co, and B of 99.9% of purity. While teaching the atmosphere-heat-treatment furnace and supplying the hydrogen gas of 1atm after fracturing said piece of casting below on 50mm square, by making it the back vacuum which it heated [vacuum] to 500 degrees C and made hydrogen absorb, performed the dehydrogenation, it was made to collapse by hydrogen absorption, and coarse grinding was carried out to the mean particle diameter of 100 micrometers. This Sm-Fe-B-Cr system magnetism powder was taught to the atmosphere-heat-treatment furnace, and was heat-treated in 460 degrees C for 7 hours in the mixed air current of ammonia partial pressure 0.35atm and hydrogen gas 0.65atm. Then, annealing was performed for 30 minutes at 400 degrees C in the hydrogen gas air current. the presentation of the obtained nitride fine particles -- atomic % display -- $\text{Sm}_{9.4}\text{Fe}_{67.1}\text{Co}_{4.0}\text{B}_{2.0}\text{Cr}_{4.5}\text{N}_{18.5}\text{H}_{2.5}$ and saturation magnetization (σ) -- 120 emu/g and iH_c -- 9 -- the temperature characteristic (η) of kOe(s) and iH_c was -0.34%/degree C. the place which observed this magnet powder with the electron microscope -- $\text{Sm}_3(\text{Fe}, \text{Cr}, \text{B})_{29}\text{Alu}_3\text{Cr}$ with a magnitude of dozens of nm -- the rich sludge was accepted.

[0056] (Examples 47-53) In order to evaluate a bond magnet property, after choosing the thing of the presentation shown in Table 8 from the magnet powder produced in the above-mentioned example and mixing these with an epoxy resin, it pressed by press ** 10 ton/cm² all over the magnetic field of 10kOe, 140 degrees C and heat treatment of 1 hour were further performed for hardening, and the isotropic bond magnet was produced. The magnetic properties of these isotropic bond magnets were shown in Table 8.

[0057]

[Table 8]

	希土類磁石粉末組成 (原子%)	平均粒径 (μm)	Br (kG)	bHc (KOe)	η (%/°C)	(BH)max (MG0e)
実施例 4 7	Sm8.3Fe bal B2.0Ti3.0N12.1	10	9.0	6.2	-0.38	12.5
実施例 4 8	Sm8.4Fe bal B2.0Ti3.2N12.5	70	8.9	6.1	-0.37	12.8
実施例 4 9	Sm8.2Fe bal B2.0Ti3.0N12.3	250	9.0	6.8	-0.39	12.9
実施例 5 0	Sm8.2Fe bal B2.0Ti3.0N11.9	500	9.1	5.9	-0.40	12.0
実施例 5 1	Sm6.2Pr2.0Fe bal B2.0Ti4.0 N12.3	70	8.5	6.8	-0.38	12.2
実施例 5 2	Sm8.3Fe bal B2.0Ti3.0N12.1 H0.5O1.1	170	9.2	6.3	-0.36	13.1
実施例 5 3	Sm8.3Fe bal B2.0Cr3.6Nb7.2 N10.4	220	8.7	6.1	-0.38	12.4

[0058] Table 8 shows that the isotropic bond magnet of this invention has the good magnet property.

[0059] Each Curie temperature of the magnet powder of each above-mentioned example had the good value of 480 ± 20 degrees C.

[0060]

[Effect of the Invention] While being able to offer easily rare earth magnet powder with the high temperature coefficient (η) of iHc and iHc covering the mean particle diameter of 20-500 micrometers, a rare earth bond magnet with the outstanding oxidation resistance and thermal resistance can be offered easily, and it is industrial very useful.

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最終頁に続く

(54) 【発明の名称】 希土類磁石材料およびその製造方法ならびにそれを用いた希土類ボンド磁石

(57) 【要約】

【課題】 $i H_c$ が大きいとともに従来に比べて $i H_c$ の温度係数 (η) が小さい熱安定性に優れた希土類磁石材料およびその製造方法ならびにそれを用いた希土類ボンド磁石を提供する。

【解決手段】 成分組成が $R_\alpha Fe_{100-(\alpha+\beta+\gamma+\delta)}$ $M_\beta B_\gamma N_\delta$ であり、単斜晶および／または六方晶の結晶構造を有した $R_3 (Fe, M, B)_{29} N_\gamma$ を主相として含み、前記 R は Y を含めた希土類元素のいずれか1種または2種以上であり、前記 M は $Al, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, W$ のいずれか1種または2種以上からなり、前記 $\alpha, \beta, \gamma, \delta$ は原子百分率で下記の範囲にあることを特徴とする希土類磁石材料。

 $5 \leq \alpha \leq 18$ $1 \leq \beta \leq 50$ $0.1 \leq \gamma \leq 5$ $4 \leq \delta \leq 30$

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【特許請求の範囲】

【請求項1】 成分組成が $R\alpha Fe_{100-(\alpha+\beta+\gamma+\delta)}M\beta B\gamma N\delta$ であり、単斜晶および／または六方晶の結晶構造を有した $R3(Fe, M, B)29Ny$ を主相として含み、前記 R は Y を含めた希土類元素のいずれか1種または2種以上であり、前記 M は $Al, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, W$ のいずれか1種または2種以上からなり、前記 $\alpha, \beta, \gamma, \delta$ は原子百分率で下記の範囲にあることを特徴とする希土類磁石材料。

$$5 \leq \alpha \leq 18$$

$$1 \leq \beta \leq 50$$

$$0.1 \leq \gamma \leq 5$$

$$4 \leq \delta \leq 30$$

【請求項2】 成分組成が $R\alpha Fe_{100-(\alpha+\beta+\gamma+\delta+\epsilon+\zeta)}M\beta B\gamma N\delta H\epsilon O\zeta$ であり、単斜晶および／または六方晶の結晶構造を有した $R3(Fe, M, B)29Ny$ を主相として含み、前記 R は Y を含む希土類元素のいずれか1種または2種以上であり、前記 M は $Al, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, W$ のいずれか1種または2種以上からなり、前記 $\alpha, \beta, \gamma, \delta, \epsilon, \zeta$ は原子百分率で下記の範囲にあることを特徴とする希土類磁石材料。

$$5 \leq \alpha \leq 18$$

$$1 \leq \beta \leq 50$$

$$0.1 \leq \gamma \leq 5$$

$$4 \leq \delta \leq 30$$

$$0.5 \leq \epsilon \leq 10$$

$$1 \leq \zeta \leq 5$$

【請求項3】 Fe 成分の0.01～30原子%を Co および／または Ni で置換したことを特徴とする請求項1または2に記載の希土類磁石材料。

【請求項4】 R 成分の50原子%以上が Sm であることを特徴とする請求項1乃至3のいずれかに記載の希土類磁石材料。

【請求項5】 希土類磁石材料の平均粒径が $20\mu m$ 以上 $500\mu m$ 以下であることを特徴とする請求項1乃至4のいずれかに記載の希土類磁石材料。

【請求項6】 $R3(Fe, M, B)29Ny$ 相の結晶粒内に M 元素または M 化合物が析出した組織を有することを特徴とする請求項1乃至5のいずれかに記載の希土類磁石材料。

【請求項7】 希土類磁石材料における $R3(Fe, M, B)29Ny$ 相の存在比率が60体積%以上であることを特徴とする請求項1乃至6のいずれかに記載の希土類磁石材料。

【請求項8】 その磁石粉末が高分子重合体、純金属、合金のいずれかにより結合されてボンド磁石を構成する希土類磁石材料であって、前記磁石粉末の25～100℃における固有保磁力(iHc)の温度係数(η)が一

0.45以上であるとともに、25℃における固有保磁力(iHc)が8kOe以上であることを特徴とする希土類磁石材料。

【請求項9】 成分組成が $R\alpha Fe_{100-(\alpha+\beta+\gamma+\delta)}M\beta B\gamma N\delta$ であり、単斜晶および／または六方晶の結晶構造を有した $R3(Fe, M, B)29Ny$ を主相として含み、前記 R は Y を含めた希土類元素のいずれか1種または2種以上であり、前記 M は $Al, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, W$ のいずれか1種または2種以上からなり、前記 $\alpha, \beta, \gamma, \delta$ は原子百分率で下記の範囲にある希土類磁石材料の粉末を、高分子重合体、純金属、合金のいずれかのバインダーで結合した希土類ボンド磁石であって、前記ボンド磁石の25～100℃における固有保磁力(iHc)の温度係数(η)が一0.45以上であるとともに25℃における保磁力(bHc)が6kOe以上であることを特徴とする希土類ボンド磁石。

$$5 \leq \alpha \leq 18$$

$$1 \leq \beta \leq 50$$

$$0.1 \leq \gamma \leq 5$$

$$4 \leq \delta \leq 30$$

【請求項10】 成分組成が $R\alpha Fe_{100-(\alpha+\beta+\gamma+\delta+\epsilon+\zeta)}M\beta B\gamma N\delta H\epsilon O\zeta$ であり、単斜晶および／または六方晶の結晶構造を有した $R3(Fe, M, B)29Ny$ を主相として含み、前記 R は Y を含む希土類元素のいずれか1種または2種以上であり、前記 M は $Al, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, W$ のいずれか1種または2種以上からなり、前記 $\alpha, \beta, \gamma, \delta, \epsilon, \zeta$ は原子百分率で下記の範囲にある希土類磁石材料の粉末を、高分子重合体、純金属、合金のいずれかのバインダーで結合した希土類ボンド磁石であって、前記ボンド磁石の25～100℃における固有保磁力(iHc)の温度係数(η)が一0.45以上であるとともに25℃における保磁力(bHc)が6kOe以上であることを特徴とする希土類ボンド磁石。

$$5 \leq \alpha \leq 18$$

$$1 \leq \beta \leq 50$$

$$0.1 \leq \gamma \leq 5$$

$$4 \leq \delta \leq 30$$

$$0.5 \leq \epsilon \leq 10$$

$$1 \leq \zeta \leq 5$$

【請求項11】 成分組成が $R\alpha Fe_{100-(\alpha+\beta+\gamma+\delta)}M\beta B\gamma N\delta$ であり、単斜晶および／または六方晶の結晶構造を有した $R3(Fe, M, B)29Ny$ を主相として含み、前記 R は Y を含めた希土類元素のいずれか1種または2種以上であり、前記 M は $Al, Ti, V, Cr, Mn, Cu, Ga, Zr, Nb, Mo, Hf, Ta, W$ のいずれか1種または2種以上からなり、前記 $\alpha, \beta, \gamma, \delta$ は原子百分率で下記の範囲にある希土類

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磁石材料を製造するに際して、窒化処理前に700～1250℃で均質化処理を行うことを特徴とする希土類磁石材料の製造方法。

$$5 \leq \alpha \leq 18$$

$$1 \leq \beta \leq 50$$

$$0.1 \leq \gamma \leq 5$$

$$4 \leq \delta \leq 30$$

【請求項12】 成分組成が $R\alpha Fe_{100-(\alpha+\beta+\gamma+\delta+\epsilon+\zeta)}M\beta B\gamma N\delta H\epsilon O\zeta$ であり、単斜晶および／または六方晶の結晶構造を有したR3(Fe, M, B)29Nyを主相として含み、前記RはYを含む希土類元素のいずれか1種または2種以上であり、前記MはAl、Ti、V、Cr、Mn、Cu、Ga、Zr、Nb、Mo、Hf、Ta、Wのいずれか1種または2種以上からなり、前記α、β、γ、δ、ε、ζは原子百分率で下記の範囲にある希土類磁石材料を製造するに際して、窒化処理前に700～1250℃で均質化処理を行うことを特徴とする希土類磁石材料の製造方法。

$$5 \leq \alpha \leq 18$$

$$1 \leq \beta \leq 50$$

$$0.1 \leq \gamma \leq 5$$

$$4 \leq \delta \leq 30$$

$$0.5 \leq \epsilon \leq 10$$

$$1 \leq \zeta \leq 5$$

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は希土類磁石材料およびその製造方法ならびにそれを用いた希土類ボンド磁石に関するものである。

【0002】

【従来の技術】従来より、希土類ボンド磁石用磁粉として超急冷したNd-Fe-B系磁粉が多用されているが、キュリー温度が300℃前後と低く、固有保磁力(以後*i*Hcと記す)の温度係数(η)が大きいために高温での使用が制限されてきた。最近、Sm2Fe17化合物が窒素を吸蔵することによりNd2Fe14B化合物よりも160℃も高い470℃というキュリー温度を示すとともに、その異方性磁界もNd2Fe14B化合物の異方性磁界(75kOe)を大きく上回る260kOeになることが報告され、ボンド磁石用磁粉として工業化が検討されている。Sm2Fe17の窒化物Sm2Fe17Nxはガス窒化法等で作製されるが、Sm2Fe17Nx磁粉の粒径を数μm程度にしないと5kOe以上の高い保磁力が得られないとともに、この粒径の磁粉は容易に酸化してその磁石特性を劣化させ、かつ急激な酸化にともなう発火の危険性を伴うので現在のところ実用化が困難である。このSm2Fe17Nx磁粉は粒径が数μmであるのでボンド磁石に圧縮成形する際、成形体密度を上げることができず高エネルギー積の希土類ボンド磁石を得られないとともに、成形性が非常に悪く作業効率を著しく低下

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せるという問題がある。また、メカニカルアロイング法などの特殊な製造方法で高い保磁力が得られることが報告されているが、この方法は実験室規模の少量生産に適するものの、コストパフォーマンスの点で劣るため量産に至っていない。さらに、Sm2Fe17Nx窒化物以外にもThMn12型の結晶構造を有したNd(Fe, M)12Nx合金(MはV、Ti、Mn、Mo等の遷移金属)や、TbCu7型の結晶構造を有したSmFe7Nx合金等が検討されているが、磁気特性の点で不十分であったり生産性が悪く高コストになる等の理由で実用化されていない。

【0003】Collocottらによって最初にProc. 12th Int. Workshop on RE Magnets and Applications, Canberra, pp. 437-444, 1992 (unpublished)に報告されたR3(Fe, M)29合金もその窒化物R3(Fe, M)29Nyが一軸磁気異方性を示すことから永久磁石材料として有望であることが示唆されている。この合金系のSm3(Fe, Ti)29Ny合金をボールミルで平均粒径15μmまで微粉砕することによって保磁力を高められることがBo-Ping Hu et al. (J. Phys.: Condens. Matter 6(1994)L197-L200)によって報告されている。しかし、このものも平均粒径が15μmと小さいため成形体密度の不足や成形性が悪い等の理由でボンド磁石用磁粉として実用化することは難しい。一方、Margarian et al. は、J. Appl. Phys. 76(1994)6135-6155においてこのR3(Fe, M)29合金は非常に不安定で900～1000℃で他の相に分解してしまうと報告している。したがってこのR3(Fe, M)29合金は高温でのみ安定に存在する相と言える。本発明者らの実験によってもこのことは確認されており、さらに付け加えるとこのR3(Fe, M)29合金の単相を得ることは非常に難しく、ThMn12型やTh2Zn17型の結晶構造を有するR(Fe, M)合金やFe-M合金が非常に生成し易いのである。

【0004】また、特開平8-111305ではこのR3(Fe, M)29合金を用いてNまたはCを導入することにより粗粉末で高い保磁力が得られることが開示され、R3(Fe, M)29母合金を作製したのちにアンモニアガスあるいはメタンガスを用いて窒化あるいは浸炭処理を行うことにより上記のSm2Fe17化合物にN、Cを導入したときと同様にN、CがR3(Fe, M)29相の格子間距離を拡げて自発磁化およびキュリー温度が増大する。すなわち、格子間距離を拡げる目的でNあるいはCの導入がなされており、各々の元素の単独添加でもこの目的は達成可能である。NとCの両者を用いる場合には母合金にCを含有させた後Nを導入する方法も考えられるが、特開平8-111305ではCが窒化処理前の母合金に含まれそれによってR3(Fe, M, C)29相を安定化させるとかあるいは母合金中のR3(Fe, M, C)29相の割合を高める役割を果たしているもので

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はない。

【0005】

【発明が解決しようとする課題】ボンド磁石の耐熱性を向上するためには*i Hc*の絶対値を高くするとともに*i Hc*の温度係数(η)を小さくする必要があるので、異方性磁界が大きいとともにキュリー温度が高い希土類磁石粉末が必要である。前述したようにR-Fe-N系合金は従来のNd-Fe-B系合金よりも異方性磁界が大きくかつキュリー温度が高いことから*i Hc*の温度係数

(η)の小さい材料として期待されているが、R-Fe-N系合金で5 kOe以上の高い*i Hc*を得るには上記の通り数 μm の微粉状にする必要があり、この微粉末は通常工業生産で用いられている6~10 ton/cm²程度の成形圧力ではボンド磁石の成形体密度を十分に上げることができず高エネルギー積を獲得できないとともに、酸化し易く不安定でさらに成形性が非常に悪いものである。上記従来の問題を踏まえて、本発明の課題は*i Hc*が大きいとともに従来に比べて*i Hc*の温度係数

(η)が小さい熱安定性に優れた希土類磁石材料およびその製造方法ならびにそれを用いた希土類ボンド磁石を提供することである。本発明者らは鋭意検討の結果、異方性磁界およびキュリー温度が高い独自の磁石粉末をボンド磁石用に開発したもので、本発明によれば粒径が大きい粗粉末でもって高*i Hc*でかつ*i Hc*の温度係数

(η)が小さい希土類磁石材料を提供できるという優れた特長を有している。すなわち、本発明におけるBの役割は上記のC、Nの作用とは全く異なりその主相に固溶してR₃(Fe, M, B) 29相の安定化に寄与するものである。理想的にはこの相単相で母合金を構成可能であり、その母合金にNを導入することにより従来のR₃

(Fe, M) 29主相の窒化物に比べて*i Hc*が大でかつ*i Hc*の温度係数(η)が小であるとともにキュリー温度が約480±20℃と高く、高エネルギー積の希土類磁石材料および希土類ボンド磁石を提供可能である。

【0006】

【課題を解決するための手段】本発明者らはボンド磁石の成形工程における成形容易性およびそれに用いた希土類磁石粉末の良好な耐酸化性と高磁石特性とを確保する目的で、平均粒径が20 μm 以上の粗粉で高い*i Hc*と飽和磁化、および低い*i Hc*の温度係数(η)を有するR-Fe-N系磁石粉末を得るために種々のR-Fe-N系合金に添加物を加えた組成を鋭意検討した結果、R-Fe-M-B-N系磁石材料を見出し本発明を成すに至った。すなわち、本発明は、成分組成が $R\alpha\text{Fe}100-(\alpha+\beta+\gamma+\delta)M\beta B\gamma N\delta$ であり、単斜晶および/または六方晶の結晶構造を有したR₃(Fe, M, B) 29Nyを主相として含み、前記RはYを含めた希土類元素のいずれか1種または2種以上であり、前記MはAl、Ti、V、Cr、Mn、Cu、Ga、Zr、Nb、Mo、Hf、Ta、Wのいずれか1種または2種以上からな

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り、前記 α 、 β 、 γ 、 δ は原子百分率で下記の範囲にあることを特徴とする希土類磁石材料である。

 $5 \leq \alpha \leq 18$ $1 \leq \beta \leq 50$ $0.1 \leq \gamma \leq 5$ $4 \leq \delta \leq 30$

【0007】上記希土類元素RとしてはY、La、Ce、Pr、Nd、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm、Yb、Luのいずれか1種または2種以上を含めばよく、ミッシュメタルやジジム等の2種以上の希土類元素の混合物を用いてもよい。好ましい希土類元素RとしてはY、Ce、Pr、Nd、Sm、Gd、Dy、Erのいずれか1種または2種以上であり、さらに好ましくはY、Ce、Pr、Nd、Smのいずれか1種または2種以上であり、特に好ましいのはSmである。ここで、希土類元素Rは工業的生産により入手可能な純度でよく、製造上混入が避けられないO、H、C、Al、Si、Na、Mg、Ca等の不純物元素が含有されていてもよい。本発明の希土類磁石材料はR成分を5~18原子%含有する。R成分が5原子%未満になると鉄成分を多く含む軟磁性相の析出を促進して*i Hc*が低下し、18原子%を越えると非磁性のRリッチ化合物が析出して飽和磁束密度を低下させるので好ましくない。さらに好ましいR成分範囲は6~12原子%である。

【0008】Feは47原子%以上を含有することが好ましい。Feが47原子%未満では飽和磁化が小さくなり好ましくない。

【0009】上記M元素はB元素との共存下においてR₃(Fe, M, B) 29相を安定させ、かつ後述するように窒化時の分解温度を上昇させるのに有効である。R₃(Fe, M, B) 29相を生成させるに要するM元素の添加量はM元素の種類毎に異なるが、M元素のいずれでも50原子%を越えて添加すると、ThMn12型の結晶構造を有するR(Fe, M, B) 12相の生成率が大きくなり*i Hc*が急激に低下する。M元素が1原子%未満ではTh₂Zn17型の結晶構造を有するR₂(Fe, M, B) 17相の生成率が大きくなりR₃(Fe, M, B) 29相の存在比率が相対的に低下し、いずれも好ましくない。よってM元素の好ましい添加量は1~50原子%である。M元素のうちで好ましい元素はTi、Mn、Cr、Zr、Vのいずれか1種または2種以上である。R₃(Fe, M, B) 29相を生成するにはM元素が必須であるが、Bを含有しないR₃(Fe, M) 29相は上述の通り不安定であり、均質化処理や窒化処理時に他の相に分解し易いのでR₃(Fe, M) 29Ny相単相の希土類磁石粉末を得ることが非常に困難である。

【0010】窒化に供する母合金中のR₃(Fe, M) 29相の割合が低いと窒化してもその窒化物R₃(Fe, M) 29Nyの生成比率が低いので良好な磁石特性を得られない。この点を考慮して本発明者らは、上記Bおよび

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M元素が共存した場合に60体積%以上好ましくは75体積%以上の単相に近い安定なR3(Fe, M, B)29相が得られることを見出した。したがって、窒化処理前の母合金においてR3(Fe, M, B)29相の存在割合を飛躍的に高めることができ、窒化処理後の希土類磁石材料中に占めるR3(Fe, M, B)29Ny相の存在割合が従来のBを含まないR3(Fe, M)29相を窒化した場合に比べて格段に増大するので高磁束密度と、高保磁力を発生させることが可能となる。本発明においてBの好ましい含有量は0.1~5原子%である。Bが0.1原子%未満および5原子%を越えるとR3(Fe, M, B)29Ny窒化物相が不安定となり他の相へ分解し易くなるので好ましくない。すなわち、R3(Fe, M, B)29相を安定化する作用は上記B添加量の範囲にあるときに発揮されるのである。このような微量のB添加による有効性はこれまで知られていない。例えば、Sm2Fe17合金にB、C、Nを加えていったときの固溶限について、H.Horiuchi et al (J.Alloys.Comp.222(1995)131-135)の報告によればCは約7原子%、Nは約14原子%まで固溶するのに対しBは約1原子%までしか固溶せず、Bの固溶による格子の拡がりおよびキュリー温度の上昇はごくわずかであるとされている。これらはC、N、Bをいずれも侵入型の元素として考えこれらの元素の導入により格子間距離の拡張をねらったものであり、本発明のように微量のB添加により上記主相の安定化を図るという手法はこれまで見出されていなかった。本発明におけるBとM元素の共存効果は上記の通り母合金中のR3(Fe, M, B)29相の存在割合を高めて、均質化処理や窒化処理において α Fe等の他相への分解を抑制する効果を有している。例えば、従来では均質化処理においてR3(Fe, M)29相が安定な加熱温度範囲が狭く、また窒化温度が高い場合や長時間窒化を行う場合は一度生成した窒化相：R3(Fe, M)29Nyが不安定で α Fe等が生成してしまい得られた磁石材料の保磁力が大きく低下するが、本発明の場合はBを適量添加することで広い均質化処理温度および窒化温度の範囲を採用可能で、生産性の向上、希土類磁石材料の磁石品質の安定化にも有効である。さらに、B添加によってR3(Fe, M, B)29相の安定化に寄与するM元素の含有範囲が従来のR3(Fe, M)29相の場合に比べて広

【0011】R3(Fe, M, B)29相に導入される窒素Nは4~30原子%とすることが好ましい。窒素Nが4原子%未満では磁化が低くなるとともに、30原子%を越えると保磁力を向上させることが困難である。より好ましい窒素Nの含有量は10~20原子%である。

【0012】また、Feの0.01~30原子%をCoおよび/またはNiで置換することが好ましく、Coお

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よび/またはNiの導入によりキュリー温度が上昇するとともにiHcの温度係数(η)ならびに耐酸化性も向上する効果がある。Coおよび/またはNiによるFe置換量のより好ましい範囲は1~20原子%である。置換量が30原子%を越えると飽和磁束密度およびiHcの顕著な低下を招来するとともに、1原子%未満ではCoおよび/またはNiの添加効果が認められない。

【0013】本発明のR成分の50原子%以上好ましくは70%以上をSmとすることにより、際立って高いiHcが得られるので好ましい。また、本発明の希土類磁石材料の平均粒径を20~500 μ mとすることが好ましい。20 μ m未満では酸化による品質劣化および成形性劣化が顕著となり、500 μ mを超えると通常の窒化条件では窒素の拡散距離が粒子径の大きな粉末粒子に対して不十分となり易く粉末粒子内に均一に窒化物が形成されない不具合を生じて好ましくない。より好ましい平均粒径の範囲は30~400 μ mである。また、R3(Fe, M, B)29Ny相の結晶粒内にM元素またはM化合物が析出した組織を有した場合に高いiHcと、低いiHcの温度係数(η)を得ることができる。

【0014】また、本発明によれば希土類磁石材料におけるR3(Fe, M, B)29Ny相の存在比率が60体積%好ましくは75体積%のものを容易に提供可能である。

【0015】また、本発明は、その磁石粉末が高分子重合体、純金属、合金のいずれかにより結合されてボンド磁石を構成する希土類磁石材料であって、前記磁石粉末の25~100℃における固有保磁力(iHc)の温度係数(η)が-0.45以上であるとともに、25℃における固有保磁力(iHc)が8kOe以上であることを特徴とする希土類磁石材料である。

【0016】また、本発明は、成分組成が $R\alpha Fe_{100-(\alpha+\beta+\gamma+\delta+\epsilon+\zeta)}M\beta B\gamma N\delta H\epsilon O\zeta$ であり、単斜晶および/または六方晶の結晶構造を有したR3(Fe, M, B)29Nyを主相として含み、前記RはYを含む希土類元素のいずれか1種または2種以上であり、前記MはAl、Ti、V、Cr、Mn、Cu、Ga、Zr、Nb、Mo、Hf、Ta、Wのいずれか1種または2種以上からなり、前記 α 、 β 、 γ 、 δ 、 ϵ 、 ζ は原子百分率で下記の範囲にあることを特徴とする希土類磁石材料である。

$$5 \leq \alpha \leq 18$$

$$1 \leq \beta \leq 50$$

$$0.1 \leq \gamma \leq 5$$

$$4 \leq \delta \leq 30$$

$$0.5 \leq \epsilon \leq 10$$

$$1 \leq \zeta \leq 5$$

本発明の希土類磁石材料は窒化に供するまでの工程で窒素処理を施すことや粉碎粒度を調整することによって、最終の窒化磁性粉において水素Hを0.5~10原子%

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および/または酸素Oを1~5原子%含ませることができる。水素を0.5~10原子%含んだ場合は窒化の効率を向上させる効果がある。これは既にR3(Fe, M, B)29相に存在している水素を窒素が置き換えていくために短時間で窒素がR3(Fe, M, B)29相に拡散できるためと考えられる。しかし、水素が0.5原子%未満ではその効果が認められず、10原子%を越えると飽和磁化が減少するとともに拡散した水素が余剰となるので化学的に不安定になってしまう。次に、酸素は1~5原子%含有した場合にiHcの温度係数(η)を大きくする効果が認められる。酸素が1原子%未満ではその有効性は認められず、5原子%を越えると磁化およびiHcの低下が顕著になるので好ましくない。

【0017】また、本発明は上記の特長ある磁石粉末を高分子重合体、純金属、合金のいずれかのバインダーで結合した希土類ボンド磁石であって、前記希土類ボンド磁石の25~100℃における固有保磁力(iHc)の温度係数(η)が-0.45以上であるとともに、25℃における保磁力(bHc)が6kOe以上であることを特徴とする希土類ボンド磁石である。

【0018】また、本発明は、成分組成が $R\alpha Fe_{100-(\alpha+\beta+\gamma+\delta)}M\beta B\gamma N\delta$ であり、単斜晶および/または六方晶の結晶構造を有したR3(Fe, M, B)29Nyを主相として含み、前記RはYを含めた希土類元素のいずれか1種または2種以上であり、前記MはAl、Ti、V、Cr、Mn、Cu、Ga、Zr、Nb、Mo、Hf、Ta、Wのいずれか1種または2種以上からなり、前記 α 、 β 、 γ 、 δ は原子百分率で下記の範囲にある希土類磁石材料を製造するに際して、窒化処理前に700~1250℃で均質化処理を行うことを特徴とする希土類磁石材料の製造方法である。

$$5 \leq \alpha \leq 18$$

$$1 \leq \beta \leq 50$$

$$0.1 \leq \gamma \leq 5$$

$$4 \leq \delta \leq 30$$

【0019】また、本発明は、成分組成が $R\alpha Fe_{100-(\alpha+\beta+\gamma+\delta+\epsilon+\zeta)}M\beta B\gamma N\delta H\epsilon O\zeta$ であり、単斜晶および/または六方晶の結晶構造を有したR3(Fe, M, B)29Nyを主相として含み、前記RはYを含む希土類元素のいずれか1種または2種以上であり、前記MはAl、Ti、V、Cr、Mn、Cu、Ga、Zr、Nb、Mo、Hf、Ta、Wのいずれか1種または2種以上からなり、前記 α 、 β 、 γ 、 δ 、 ϵ 、 ζ は原子百分率で下記の範囲にある希土類磁石材料を製造するに際して、窒化処理前に700~1250℃で均質化処理を行うことを特徴とする希土類磁石材料の製造方法である。

【0020】

【発明の実施の形態】以下本発明を詳説する。本発明の希土類磁石材料は単斜晶および/または六方晶の結晶構

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造を有するR3(Fe, M, B)29Ny相の単相のものが理想的であるが、この主相の他に磁石特性に寄与しない他の化合物(以後副相と呼ぶ)を含有することができる。この副相としてTh2Zn17型、TbCu7型、ThMn12型などの結晶構造を有するR-Fe-M-B-N系磁性化合物を含んでいてもよいが、上記の通り本発明の主相の含有比率は60体積%以上が好ましく、75体積%以上がより好ましい。R3(Fe, M, B)29Ny主相は、母合金全部または母合金を主に構成するR3

(Fe, M, B)29相の結晶格子間に窒素が侵入してその結晶格子が膨張することによって得られるが、その結晶構造はR3(Fe, M, B)29相とほぼ同じ対称性を有する。例えば母合金粉末として原子%表示でSm9.4Fe84.0B2.0Ti4.5の組成のものを選んだ場合、窒素を導入することによって結晶磁気異方性が面内異方性から一軸異方性に変化し永久磁石材料として好適なものになる。

【0021】本発明にかかる希土類ボンド磁石は、上記希土類磁石材料を高分子重合体、純金属、合金等のいずれかのバインダーで固めてなるものであるが、高分子重合体としてはエポキシ樹脂やフェノール樹脂等に代表される熱硬化樹脂またはポリアミド樹脂やEEA樹脂等の熱可塑性樹脂または合成ゴムや天然ゴム等の公知のものをを用い得る。また、純金属または合金としては亜鉛や錫などの公知の低融点金属や低融点合金を用いることができる。また、希土類ボンド磁石の成形方法としては圧縮成形や射出成形などの公知の成形方法を採用できる。

【0022】本発明によれば、R3(Fe, M, B)29Ny主相の存在比率の高い希土類磁石材料を容易かつ安定に作製できるので、キュリー温度が約480±20℃と高く熱安定性に優れるとともに平均粒径で20~500μmの幅広い粒径にわたって略一定の高いiHcと低いiHcの温度係数(η)を有した希土類磁石粉末を提供できると同時に、高磁石特性の等方性や異方性ボンド磁石を容易に製作することができる。

【0023】次に、本発明の代表的な製造工程を説明する。

【0024】(母合金の調整)本発明の磁石材料はBとM元素との複合添加により窒化処理に供するR-Fe-M-B系母合金中のR3(Fe, M, B)29相の含有比率を高めたものである。R-Fe-M-B系母合金は例えば高周波溶解法、アーク溶解法、超急冷法、ストリップキャスト法、ガスアトマイズ法、還元拡散法、メカニカルアロイング法等のいずれかを用いて合金化される。上記方法で得た合金を水素雰囲気下で加熱保持し、続いて脱水素処理を行い水素化合物を分解させて母合金相に再結合させてもよい。ここで、高周波溶解法またはアーク溶解法を用いた場合には上記合金が凝固する際に α Feを主成分とする軟磁性相が析出し易いが、この軟磁性相は窒化処理後も残留し保磁力を低下させる要因となるので好ま

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しくない。この軟磁性相の生成を抑えるには溶製した母合金を真空中またはアルゴンガス雰囲気中で700～1250℃×0.5～100時間の加熱条件で均質化処理することが望ましい。従来のR3 (Fe, M) 29相は上記の通り900～1000℃で分解するのに対し、本発明では700～1250℃という広い均質化処理温度を許容できる利点を有している。

【0025】(粉碎) 上記方法で溶製した母合金塊またはメカニカルアロイングしたものを直接窒化することも可能であるが、窒化処理物のサイズが大きいと窒化処理時間が長くなるので粗粉碎を行って平均粒径で500μm以下に粗粉碎後に窒化することが望ましい。粗粉碎は例えばディスクミル、パンタムミル、ジョークラッシャー、ボールミルなどの粉碎機を用いて行うことができる。また母合金に水素を吸蔵させた後に上記粉碎機で粗粉碎する方法や、水素の吸蔵と放出とを繰り返して粗粉碎する方法を用いてもよい。さらに粗粉碎の後、篩で分級し窒化すると母合金中に均質な窒化物の主相を形成できるので好ましく、例えば、窒化処理前に20μm～100μm未満、100μm～200μm未満、200μm～300μm未満、300μm～400μm未満、400μm～500μm未満というように篩分すると窒化処理後の磁石粉末がほぼこれらの篩分粒径になっており、上記の均質な窒化物形成効果とともにボンド磁石形状に応じて要求される成形性の難易に合わせてこれらの略篩分粒径の磁石粉末を適宜採用できるので実用上好適なものである。さらに、粗粉碎後、アルゴンガス雰囲気または真空中で500～1000℃×0.5～100時間でアニールすると磁石特性が向上するが、この効果は粗粉碎により導入された歪みが緩和されるためと考えられる。

【0026】(窒化) 本発明では公知の窒化処理方法(例えば、ガス窒化法、イオン窒化法等。)を採用できる。一例として、ガス窒化法について説明する。ガス窒化法は窒素ガス、アンモニアガス、窒素ガスと水素ガスの混合ガス、アンモニアガスと水素ガスの混合ガス等のいずれかを上記母合金塊または上記母合金の粗粉碎粉に接触させて結晶格子内に窒素を導入する工程である。窒化反応は上記のようなガス種を選ぶこと、加熱温度、加熱時間、ガス圧力により制御できる。このうち加熱温度は母合金組成によって異なるが300～650℃が好ましい。母合金の種類によらず300℃未満であると窒化がほとんど進行せず、また650℃を超えると一旦生成した窒化物が分解してαFeなどの軟磁性相が生成するので好ましくない。窒化後にさらにアルゴン等の不活性ガス中あるいは真空中あるいは水素ガス中で300～600℃×0.5～50時間アニールすると保磁力、iHc、飽和磁化等が向上する場合がある。これはアニールにより窒素が母合金の結晶粒子内にさらに拡散して主相の窒化物相の割合が増加することや粉末粒子内に均一に

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窒化物が形成されて行くためと思われる。

【0027】(磁場成形) 上記のようにして作成した本発明の希土類磁石材料粉末を用いて異方性ボンド磁石を作製するには、その磁石粉末と熱硬化性樹脂または低融点金属(低融点合金)のバインダーとを適正比率で混合した後例えば10kOe以上の磁場中で圧縮成形したり、その磁石粉末と熱可塑性樹脂とを適正比率で配合し加熱混練して得たコンパウンドを例えば10kOe以上の磁場中で射出成形する方法を採用できる。等方性のボンド磁石を作製する場合には本発明の希土類磁石材料粉末を上記樹脂または金属(合金)のバインダー粉末と適正比率で配合後均一化のために混合した後、磁場無しで成形体を形成し、その後加熱硬化処理を行えばよい。

【0028】(着磁) 上記のボンド磁石に十分な磁力を付与するための着磁作業は好ましくは15kOe以上、より好ましくは20kOe以上の着磁磁場で行うことが一般的である。

【0029】次に本発明の各物性値の評価方法について具体的に説明する。

20 (平均粒径の測定) 上記磁石材料粉末の平均粒径はレーザー回折式粒度分布測定装置(GALAI社製、CIS-1型)を用いてその体積相当径分布を測定し、その分布曲線より平均粒径を求めた。

(磁気特性の測定) 上記磁石材料のiHc、飽和磁化(σ)はその磁石粉末の所定量を樹脂に混ぜて銅容器に詰め込み、振動試料型磁力計(東英工業(株)製のVSM-3型)を用いて測定した。ボンド磁石のiHc、残留磁束密度(Br)、iHcの温度係数(η)は自記磁束計(東英工業(株)製TRF-5H)を用いて測定した。

30 【0030】(成分分析) 上記磁石材料の構成元素のうち、窒素、水素、酸素はN、O、Hガス分析装置((株)堀場製作所製のEMGA1300)を用いてガスクロマトグラフィー熱伝導検出法により分析した。また、Sm等の希土類元素はシュウ酸塩重量法、Feは2クロム酸カリウム容量法、Ti等のM元素とBは誘導結合型プラズマ発光分析法により分析した。

40 【0031】(耐酸化性の評価) 希土類磁石粉末を大気中で100℃×相対湿度90%に保持された恒温槽内に168時間放置した後、取り出して25℃でiHcを測定し、この恒温槽に入れる前の25℃におけるiHcと比較して減少率である耐酸化性を求めた。すなわち、

(耐酸化性) = (恒温槽処理後の磁石粉末の25℃におけるiHc) ÷ (恒温槽処理前の磁石粉末の25℃におけるiHc) × 100 (%) で定義した値である。この値が小さいほど耐酸化性に優れるものである。

【0032】次に、本発明を実施例により説明するがこれらにより本発明が限定されるものではない。

(実施例1～12) B添加量と磁石特性との相関を見るため表1に示される希土類磁石粉末を作製し評価した。

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まず、純度99.9%のSm、Fe、Ti、Bを用いて表1の実施例1～12の窒化物磁石粉末に対応した母合金組成になるように各々配合し、アルゴンガス雰囲気の高周波溶解炉で溶解して実施例1～12に対応した各母合金を溶製した。その後、アルゴンガス雰囲気中で1150℃、20時間の均質化処理を行い、続いてこの母合金塊をジョークラッシャーとディスクミルを用いて粉砕した。これらの母合金粉末のX線回折をCu-K α 線を用いて行ったところ回折線はすべてR3 (Fe, M, B) 29相として指数付けできることを確認した。次に上記各母合金粉末を雰囲気加熱炉に仕込み450℃において窒素ガス1atm気流中で5時間加熱保持し窒化処理を行い、続いてアルゴン気流中で420℃で1時間アニールした。この窒化処理した各粉末のX線回折を行ったところ母合金で得られたR3 (Fe, M, B) 29相のX線回折パターンより低回折角度側にシフトしており、N原子が母合金結晶に侵入することによってその結*

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* 晶格子が広がったことが確認できた。こうして得られた実施例1～12の窒化物磁石粉末の組成、平均粒径、25℃における飽和磁化の強さ(σ)およびiHc、25～100℃におけるiHcの温度係数(η)を測定した結果を表1に示した。ここで、下記各実施例および各比較例における各測定は全て表1の測定と同条件で行っている。

【0033】(比較例1～6)表1に示すようにBを含有しない母合金組成とするとともに平均粒径を変えた以外は実施例1と同様にして表1に示される比較例1～6の窒化物磁石粉末を作製し評価した。Bを含有していないこの比較例1～6の窒化処理前の母合金粉末にはTh2Zn17型のSm2 (Fe, Ti, B) 17相と α Feおよび/またはFe-Ti相の生成が認められた。

【0034】

【表1】

	希土類磁石粉末組成 (原子%)	平均粒径 (μ m)	σ (emu/g)	iHc (kOe)	η (%/℃)
実施例1	Sm8.2FeBaB2.0Ti4.0N12.7	20	129	8.1	-0.37
実施例2	Sm8.2FeBaB2.0Ti4.1N12.9	40	133	11.5	-0.35
実施例3	Sm8.4FeBaB2.0Ti4.2N12.5	70	132	12.9	-0.34
実施例4	Sm8.3FeBaB2.0Ti4.1N12.7	140	132	12.3	-0.33
実施例5	Sm8.2FeBaB2.0Ti4.0N12.3	260	130	11.9	-0.33
実施例6	Sm8.3FeBaB2.0Ti4.2N12.4	420	128	11.3	-0.32
実施例7	Sm8.3FeBaB2.0Ti4.2N12.4	500	131	8.0	-0.32
実施例8	Sm8.3FeBaB0.1Ti4.2N12.4	140	129	8.4	-0.39
実施例9	Sm8.3FeBaB0.5Ti4.2N12.4	140	136	11.2	-0.38
実施例10	Sm8.3FeBaB1.0Ti4.2N12.4	140	134	9.7	-0.32
実施例11	Sm8.3FeBaB3.0Ti4.2N12.4	140	130	10.8	-0.39
実施例12	Sm8.3FeBaB5.0Ti4.2N12.4	140	126	9.1	-0.39
比較例1	Sm8.3FeBaTi4.2N12.7	20	132	2.9	-0.59
比較例2	Sm8.3FeBaTi4.2N12.5	85	130	2.1	-0.57
比較例3	Sm8.3FeBaTi4.2N12.2	240	127	1.8	-0.55
比較例4	Sm8.2FeBaTi4.1N12.5	490	125	1.9	-0.54
比較例5	Sm8.3FeBaB0.05Ti4.2N12.4	130	130	2.1	-0.55
比較例6	Sm8.3FeBaB6.0Ti4.2N12.4	130	119	1.5	-0.53

【0035】表1より、BとM元素の複合添加の効果が明らかである。すなわちBを0.1～5原子%含んだ実施例1～12では平均粒径20～500 μ mにわたって

8kOe以上の高いiHcが得られているとともに、iHcの温度係数(η)も-0.45以上で良好な耐熱性を有していることがわかる。一方、Bを含まない比較例

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のものはいずれも iH_c が $3kOe$ 未満で、 iH_c の温度係数 (η) も -0.53 以下であり耐熱性に劣ることがわかる。

【0036】(実施例13～15) R成分含有量およびR成分の種類と磁石特性との相関を見るために、表2に示した磁石粉末組成にするとともに平均粒径 $72\mu m$ とした以外は上記実施例1と同様な操作によって、表2に示した磁石粉末を製作するとともに飽和磁化 (σ)、 i *

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* H_c 、 iH_c の温度係数 (η) を測定した。

(比較例7～10) 表2に示した磁石粉末組成にした以外は実施例13～15と同様にして、表2に示した磁石粉末を製作するとともに飽和磁化 (σ)、 iH_c 、 iH_c の温度係数 (η) を測定した。

【0037】

【表2】

	希土類磁石粉末組成 (原子%)	σ (emu/g)	iH_c (kOe)	η (%/°C)
実施例13	Sm8.3FeBaB2.0Ti4.0N12.1	130	8.5	-0.35
実施例14	Sm6.2Pr2.0FeBaB2.0Ti4.0N12.3	125	8.8	-0.37
実施例15	Sm5.2Pr3.1FeBaB2.0Ti4.1N12.9	122	8.1	-0.35
比較例7	Sm3.9Pr4.4FeBaB2.0Ti4.1N12.9	125	2.8	-0.63
比較例8	Sm2.2Pr6.1FeBaB2.0Ti4.1N12.9	120	1.9	-0.64
比較例9	Sm3.2FeBaB2.0Ti4.0N10.3	136	2.5	-0.59
比較例10	Sm19.3FeBaB2.0Ti4.2N12.4	89	3.1	-0.54

【0038】表2から、R成分中のSm比率が50原子%以上のときに高い iH_c と低い iH_c の温度係数 (η) が得られることがわかる。

【0039】(実施例16～20) 上記表2に続いてR成分含有量およびR成分の種類と磁石特性との相関を見るために、表3に示す磁石粉末組成にするとともに平均粒径を $130\mu m$ に変更した以外は上記実施例1と同様※30

※な操作によって表3に示す磁石粉末を得るとともに磁化、 iH_c 、 iH_c の温度係数 (η) を測定した。

(比較例11～14) 表3の磁石粉末組成とした以外は実施例16～20と同様の評価を行った。

【0040】

【表3】

	希土類磁石粉末組成 (原子%)	σ (emu/g)	iH_c (kOe)	η (%/°C)
実施例16	Sm5.0FeBaB2.0Ti4.0N12.1	136	8.2	-0.39
実施例17	Sm8.3FeBaB2.0Ti4.0N12.1	132	12.3	-0.35
実施例18	Sm6.2Pr2.0FeBaB2.0Ti4.0N12.3	125	10.8	-0.37
実施例19	Sm5.2Pr3.1FeBaB2.0Ti4.1N12.9	122	9.1	-0.36
実施例20	Sm14.9Pr3.1FeBaB2.0Ti4.1N12.9	92	10.5	-0.38
比較例11	Sm4.8FeBaB2.0Ti4.0N10.3	126	3.5	-0.31
比較例12	Sm19.3FeBaB2.0Ti4.2N12.4	105	2.1	-0.59
比較例13	Sm3.2Pr1.6FeBaB2.0Ti4.0N11.3	126	3.5	-0.50
比較例14	Sm15.5Pr3.5FeBaB2.0Ti4.2N12.4	95	3.9	-0.59

【0041】表3より、R成分中のSm比率が50原子%以上でかつR成分が5～18原子%のときに高い iH_c と低い iH_c の温度係数 (η) が得られることがわかる。

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【0042】（実施例21～24）窒素含有量と磁石特性との相関を見るために、表4に示す磁石粉末組成および平均粒径を120 μ mとした以外は上記実施例1と同様にして表4の磁石粉末を得るとともに、飽和磁化（ σ ）、iHc、iHcの温度係数（ η ）を測定した。*

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*（比較例15、16）表4の磁石粉末組成とした以外は実施例21～24と同様の評価を行った。

【0043】

【表4】

	希土類磁石粉末組成（原子%）	σ (emu/g)	iHc (kOe)	η (%/°C)
実施例21	Sm8.3FeBaB2.0Ti4.0N4.0	122	9.3	-0.39
実施例22	Sm8.3FeBaB2.0Ti4.0N15.3	131	10.8	-0.37
実施例23	Sm8.1FeBaB2.0Ti4.1N20.9	138	14.1	-0.38
実施例24	Sm8.2FeBaB2.0Ti4.1N30.0	119	9.8	-0.39
比較例15	Sm8.2FeBaB2.0Ti4.1N3.5	92	2.9	-0.49
比較例16	Sm8.2FeBaB2.0Ti4.0N32.1	106	2.5	-0.51

【0044】表4から窒素量が4～30原子%含有された実施例21～24では高いiHcと低いiHcの温度係数（ η ）が得られることがわかる。比較例15、16に示したように窒素量が5原子%よりも少ないときと30原子%よりも多いときにはiHcが低く3kOe未満の値である。

【0045】（実施例25～29）Fe成分をCoまたはNiで置換した場合の磁石特性を見るために、表5に※

※示す磁石粉末組成に変更するとともに平均粒径を170 μ mとした以外は上記実施例1と同様な操作によって、表5の磁石粉末を得るとともに、飽和磁化（ σ ）、iHc、iHcの温度係数（ η ）を測定した。

（比較例17～19）表5の磁石粉末組成とした以外は実施例25～29と同様の評価を行った。

【0046】

【表5】

	希土類磁石粉末組成（原子%）	σ (emu/g)	iHc (kOe)	η (%/°C)	耐酸化性(%)
実施例25	Sm8.3FeBaCo0.01B2.0Ti4.0N12.1	130	8.3	-0.32	-1.8
実施例26	Sm8.3FeBaCo1.0B2.0Ti4.0N12.3	128	8.2	-0.30	-0.9
実施例27	Sm8.2FeBaCo30.0B2.0Ti4.1N12.9	94	8.1	-0.30	-0.1
実施例28	Sm8.3FeBaNi1.0B2.0Ti4.0N10.3	110	8.5	-0.31	-1.2
実施例29	Sm8.3FeBaCo20.0Ni10.0B2.0Ti4.0N10.3	106	8.5	-0.31	-1.1
比較例17	Sm8.3FeBaB2.0Ti4.0N12.1	129	8.2	-0.39	-2.5
比較例18	Sm8.1FeBaCo0.005B2.0Ti4.1N12.9	131	8.2	-0.37	-2.4
比較例19	Sm8.2FeBaCo33.0B2.0Ti4.1N12.9	92	3.9	-0.52	-0.1

【0047】表5からFeの一部をCoおよび/またはNiで0.01～30原子%の範囲で置換したとき、耐酸化性が向上するとともに高いiHc、低いiHcの温度係数（ η ）が得られていることがわかる。

【0048】（実施例30～36）上記各実施例の磁石粉末に含有されるH量およびO量は不可避不純物程度であり、例えば重量%表示でH含有量が50ppm以下お

およびO含有量が5000ppm以下であった。しかし、本発明の磁石粉末は上記の通り製造条件を適宜選択することで不可避不純物含有量を超えてH、Oを含有可能である。積極的に含有させたH量、O量による影響を見るために表6に示す組成の磁石粉末を製作するとともに平均粒径を400 μ mとした以外は上記実施例1と同様な操作によって、表6の磁石粉末を得、飽和磁化（ σ ）、

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iHc、iHcの温度係数(η)を測定した。

*【0049】

(比較例20~24)表6の磁石粉末組成とした以外は

【表6】

実施例30~36と同様にして評価した。

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	希土類磁石粉末組成(原子%)	σ (emu/g)	iHc (KOe)	η (%/°C)
実施例30	Sm8.3FeBa1B2.0Ti4.0N12.1H0.5	130	8.3	-0.31
実施例31	Sm8.3FeBa1B2.0Ti4.0N12.1H5.1	128	9.2	-0.33
実施例32	Sm8.3FeBa1B2.0Ti4.0N12.1H10.0	103	9.5	-0.34
実施例33	Sm8.3FeBa1B2.0Ti4.0N12.1O1.0	125	8.6	-0.32
実施例34	Sm8.3FeBa1B2.0Ti4.0N12.1O3.0	118	8.3	-0.31
実施例35	Sm8.3FeBa1B2.0Ti4.0N12.1O5.0	102	8.8	-0.30
実施例36	Sm8.3FeBa1B2.0Ti4.0N12.1H0.5O1.0	128	8.5	-0.32
比較例20	Sm8.3FeBa1B2.0Ti4.0N12.1H0.4	130	8.5	-0.37
比較例21	Sm8.3FeBa1B2.0Ti4.0N12.1H12.0	125	8.6	-0.49
比較例22	Sm8.3FeBa1B2.0Ti4.0N12.1O0.5	129	8.5	-0.37
比較例23	Sm8.3FeBa1B2.0Ti4.0N12.1O7.0	94	3.0	-0.49
比較例24	Sm8.3FeBa1B2.0Ti4.0N12.1H12.0O7.0	90	2.9	-0.48

【0050】表6から水素が0.5~10原子%および/または酸素が1~5原子%にあるときに高いiHcと飽和磁化(σ)および低い温度係数(η)が得られることがわかる。また、水素量が0.5~10原子%および/または酸素が1~5原子%の範囲を外れた各比較例のものは特に温度係数(η)が劣化していることがわかる。

【0051】(実施例37~44)M元素の種類および含有量の磁石特性に対する影響を見るために表7に示す

磁石粉末組成にするとともに平均粒径を $170\mu\text{m}$ とした以外は上記実施例1と同様な操作によって表7の磁石粉末を得、飽和磁化(σ)、iHc、iHcの温度係数(η)を測定した。

(比較例25、26)表7の磁石粉末とした以外は実施例37~44と同様の評価を行った。

【0052】

【表7】

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	希土類磁石粉末組成 (原子%)	σ (emu/g)	i Hc (kOe)	η (%/°C)
実施例37	Sm8.3Fe61B2.0Ti1.0N12.1	132	8.3	-0.37
実施例38	Sm8.3Fe61B2.0Ti8.0N12.1	112	9.7	-0.36
比較例25	Sm8.1Fe61B2.0Ti0.5N9.9	122	3.1	-0.51
実施例39	Sm8.2Fe61B2.0Mn20.2N12.9	119	10.1	-0.38
実施例40	Sm8.2Fe61B2.0Mn50.0N12.9	92	8.1	-0.42
比較例26	Sm8.2Fe61B2.0Mn60.0N13.9	72	3.1	-0.50
実施例41	Sm8.3Fe61B2.0V10.1N11.9	120	11.9	-0.33
実施例42	Sm8.2Fe61B2.0Al4.0N10.3	126	12.5	-0.36
実施例43	Sm8.3Fe61B2.0Ti4.2Zr8.2N13.4	119	12.1	-0.34
実施例44	Sm8.3Fe61B2.0Cr3.6Nb7.2N10.4	125	10.1	-0.39

【0053】表7からM元素が1～50原子%のときに高いiHcと低いiHcの温度係数(η)が得られることがわかる。比較例24、25に示したようにM元素がこの範囲にない場合は母合金においてSm3(Fe, M, B)29相が少量しか生成せず窒化してもiHcが向上しないことがわかった。

【0054】(実施例45) M元素としてCrを添加しFeの一部をCoで置換した下記の磁石粉末組成に対応した母合金を上記実施例1と同様の溶解条件で溶製後、その母合金を酸素分圧1モル%の窒素気流中で粗粉碎し、篩いによって平均粒度125 μ mに調整した。このSm-Fe-Co-B-Cr系合金粉をアンモニア分圧0.35 atm、水素ガス分圧0.65 atmのアンモニア-水素混合ガス気流中で460°Cで5時間の窒化処理を行った後、酸素分圧10⁻⁵ atmのアルゴン気流中で1時間アニールした。得られた平均粒径74 μ mのSm_{9.4}Fe_{64.1}Co_{4.0}B_{1.0}Cr_{4.5}N_{16.5}H_{0.5}をシクロヘキサン中で30分間ボールミル粉碎した。この粉碎粉の組成は原子%表示でSm_{9.2}Fe_{64.0}Co_{4.0}B_{1.0}Cr_{4.5}N_{16.0}H_{0.5}O_{1.0}で平均粒径は36 μ mであった。この磁粉はiHcが8 kOe、iHcの温度係数(η)は-0.31%/°Cという良好な値であった。

【0055】(実施例46) 純度99.9%のSm、Fe、Co、Bを用いて下記の窒化物粉末に対応した母合金組成に配合後、アルゴンガス雰囲気下の高周波溶解炉で溶解した合金溶湯を直径300mmの銅製ロール2本

を設置した双ロール式ストリップキャスターを用いて、板厚約2mmの薄片状鑄造片を得た。前記鑄造片を50mm角以下に破断後、雰囲気熱処理炉に仕込み1 atmの水素ガスを供給するとともに500°Cまで加熱し水素を吸収させた後真空にすることにより脱水素を行い水素吸蔵によって崩壊させて平均粒径100 μ mまで粗粉碎した。このSm-Fe-B-Cr系磁性粉を雰囲気熱処理炉に仕込み460°Cにおいてアンモニア分圧0.35 atm、水素ガス0.65 atmの混合気流中で7時間加熱処理した。続いて水素ガス気流中で400°Cで30分間アニールを行った。得られた窒化物粉体の組成は原子%表示でSm_{9.4}Fe_{67.1}Co_{4.0}B_{2.0}Cr_{4.5}N_{18.5}H_{2.5}、飽和磁化(σ)は120 emu/g、iHcは9 kOe、iHcの温度特性(η)は-0.34%/°Cであった。この磁石粉末を電子顕微鏡で観察したところSm3(Fe, Cr, B)29相内に数十nmの大きさのCrリッチな析出物が認められた。

【0056】(実施例47～53) ボンド磁石特性を評価するために、上記実施例で作製した磁石粉末から表8に示す組成のものを選択し、これらをエポキシ樹脂と混合した後、10 kOeの磁場中でプレス圧10 ton/cm²で圧縮成形し、さらに硬化のため140°C、1時間の熱処理を施して等方性ボンド磁石を作製した。これらの等方性ボンド磁石の磁気特性を表8に示した。

【0057】

【表8】

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	希土類磁石粉末組成 (原子%)	平均粒径 (μm)	Br (kG)	bHc (KOe)	η (%/°C)	(BH) _{max} (MGOe)
実施例47	Sm8.3FeBa1B2.0Ti3.0N12.1	10	9.0	6.2	-0.38	12.5
実施例48	Sm8.4FeBa1B2.0Ti3.2N12.5	70	8.9	6.1	-0.37	12.8
実施例49	Sm8.2FeBa1B2.0Ti3.0N12.3	250	9.0	6.8	-0.39	12.9
実施例50	Sm8.2FeBa1B2.0Ti3.0N11.9	500	9.1	5.9	-0.40	12.0
実施例51	Sm6.2Pr2.0FeBa1B2.0Ti4.0 N12.3	70	8.5	6.8	-0.38	12.2
実施例52	Sm8.3FeBa1B2.0Ti3.0N12.1 H0.5O1.1	170	9.2	6.3	-0.36	13.1
実施例53	Sm8.3FeBa1B2.0Cr3.6Nb7.2 N10.4	220	8.7	6.1	-0.38	12.4

【0058】表8から本発明の等方性ボンド磁石が良好な磁石特性を有していることがわかる。

【0059】上記各実施例の磁石粉末のキュリー温度はいずれも $480 \pm 20^\circ\text{C}$ という良好な値を有していた。

【0060】

【発明の効果】平均粒径 $20 \sim 500 \mu\text{m}$ にわたって高い iH_c および iH_c の温度係数(η)を有した希土類磁石粉末を容易に提供できるとともに、優れた耐酸化性と耐熱性を有した希土類ボンド磁石を容易に提供でき、工業的に非常に有用なものである。

フロントページの続き

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